The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.
http://researchspace.auckland.ac.nz/feedback

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form and Deposit Licence.
A Novel Biodegradable Fe-35wt.%Mn Alloy

Produced via Powder Metallurgy

Qian Zhang

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

Department of Chemical and Materials Engineering,

The University of Auckland, New Zealand, 2015
Abstract

This doctoral project permitted to design, develop and study a degradable metallic biomaterial. Between 2011 and 2015, magnesium alloys and commercially pure iron were evaluated for their possibility for the use in biomedical areas. Their mechanical properties and degradation behaviors were not clinically well suited. Hermawan et al. investigated a series of Fe-Mn alloys via a powder metallurgical (PM) route followed by cold rolling and re-sintering cycles and found that manganese content of 35 wt% alloy was nonmagnetic and cell compatible. However, as a fully dense alloy, the degradation rate was still not satisfactory. In this doctoral project, the Fe-35wt.%Mn alloys were produced via several PM routes. This research employed three different starting powders, which were blended elemental (BE), mechanically milled (MMed) and BE powder with porogen. We aimed to develop a less dense alloy that has a higher degradation rate, suitable mechanical properties and good cell compatibility.

The Fe-35Mn alloys were firstly fabricated by a simple blend-press-sinter method. Sintering temperatures and holding times were varied to investigate their influences on the microstructure evolution, densification, corrosion behavior as well as mechanical properties. The increase of sintering temperature and holding time led to the decrease of porosity level of the sintered compacts. Among these parameters, a sintering temperature of 1200°C and a holding time of 4 hours proved to be able to produce samples with a good densification level. The change of sintering temperature and time did not affect the final phase where non-ferromagnetic austenitic $\gamma$ and martensitic $\varepsilon$ were the main phase. A satisfactory degradation rate of 1.5 to 4 mmpy was obtained; but the mechanical strength was low.

In order to enhance the mechanical properties, a mechanical milling (MMing) process was employed to obtain finer starting powder particles. The MMing parameters were investigated and ball-to-powder (B-P) ratio of 5:1 and milling time of 6 hours were identified to be able to produce the required powder. After milling, various pressing pressures using a steel die press were employed, followed by cold isostatic pressing (CIPing) at 200 MPa. Higher compaction pressure resulted in lower porosity level and CIPing further enhanced the densification. When compared with the BE powder, reducing
the powder particle size via MMing had led to a decrease in porosity to 7 ~ 12%. Hence, a significant improvement of mechanical properties was then achieved.

Porogen ammonium bicarbonate (NH₄HCO₃) particles were added to fabricate porous Fe-35Mn alloy foam which had varying degrees of porosity level. By the addition of 10 and 20 volumetric percent of NH₄HCO₃, the degradation rates of the Fe-35Mn samples with the introduction of the NH₄HCO₃ porogen were significantly accelerated when compared with the samples without NH₄HCO₃ addition. The electrochemical corrosion rates were ranging from ca. 2 to 8 mmpy in both 5% NaCl and SBF solutions. The proposed degradation mechanisms were uniform corrosion in addition to crevice corrosion. Iron ion release during a one-month’s dynamic corrosion was slightly higher than that of manganese. However the mechanical properties of these Fe-35Mn foams posed a limitation for the development of Fe-35Mn foams in the load-bearing applications.

The stress corrosion cracking (SCC) investigation in a physiological environment followed. A slow strain rate test (SSRT) method was used in order to achieve a better understanding with regard to the stress corrosion behavior. The SCC susceptibility was sensitive to the strain rate and the testing environment. A slower strain rate and a more aggressive environment resulted in a higher SCC susceptibility. The higher density level of the sintered samples led to a reduction of SCC susceptibility. Intergranular fracture was observed on the sample surface of all tested specimens. SCC cracking was initiated from crevices and pores in both BE and MMed Fe-35Mn alloy samples.

The cytocompatibility of Fe-35Mn alloys were then investigated using an indirect cell-material interaction by culturing L929 cell line in Fe and Mn ion-rich elution containing up to 1.29 and 1.12 ppm of released Fe and Mn ions. Results showed L929 mammalian cells proliferated and grew healthily in all testing extractions. It was suggested that Fe-35Mn alloys were biocompatible since no significant difference was found in the cell viability response to the material elutes.

It has to be pointed out that the simple blend-press-sinter method was able to produce a Fe-35Mn alloy that met degradation requirement. MMing could increase the samples’ mechanical strength. However the strength level is still insufficient for load-bearing applications. A further investigation of optimizing the PM parameters is needed to increase mechanical strength while maintaining sufficiently fast degradation.
Dedication

This dissertation is dedicated to my grandmother and grandfather. I will never forget you and I will always be missing you.
Acknowledgement

First of all, I would like to express my special thanks of gratitude to my chief supervisor, Prof. Peng Cao for giving me the golden opportunity to do this wonderful project. I am thankful for his guidance, advice, support (both financial and educational) and understanding. I would also like to thank my research co-supervisor, Prof. Wei Gao. Sincere thanks are also expressed to Dr. Tianping Zhu and Professor Ashvin Thambyah who are the members of advisory committee for my Ph.D study current research.

I wish to extend my appreciation to the following organizations and people for providing support: The Research Centre for Surface and Materials Science (Ms. Catherine Hobbis) for helping microstructure observations by SEM and ESEM; The workshop in the Department of Chemical and Materials Engineering (Mr. Steve Strover, Dr. Alec Asadov, Ms. Laura Liang and other technicians).

I also would like to express my special thanks to Dr. Simon Swift and Dr. Benedict Uy from the department of Molecular Medicine and Pathology. Thanks for the assistance on the whole period of biomedical experiment. I also wish to thank people in the research group who have given all forms of support: Zhigang Xu, Dr. Yuxin Wang, Dr. Shanghai Wei, Dr. Gang Chen and all other group members.

My extra special thanks to my dear friends Zhendi Yang, See Leng Tay, Dr. Xiaojin Wei, Dr. Yantao Song and Dr. Qian Xu who have given me extremely essential support both experimental and spiritual. It is all you who have colored my Ph.D life.

Last, but certainly not least, I am deeply thankful to my dear grandmother, my parents and my partner Wang Zhang for their love, support, and sacrifices. Without them, this thesis would never have been written.
# Table of Content

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>v</td>
</tr>
<tr>
<td>Table of Content</td>
<td>ix</td>
</tr>
<tr>
<td>Chapter 1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Background</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Objectives</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Thesis outline</td>
<td>3</td>
</tr>
<tr>
<td>Chapter 2 Literature Review</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Biomaterials</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Biodegradable materials</td>
<td>9</td>
</tr>
<tr>
<td>2.2.1 Biodegradable polymers</td>
<td>9</td>
</tr>
<tr>
<td>2.2.2 Biodegradable metals</td>
<td>10</td>
</tr>
<tr>
<td>2.2.3 Biodegradable Mg and Mg alloys</td>
<td>12</td>
</tr>
<tr>
<td>2.3 Biodegradable iron and its alloys</td>
<td>13</td>
</tr>
<tr>
<td>2.3.1 Pure iron</td>
<td>14</td>
</tr>
<tr>
<td>2.3.2 Alloy development by incorporating Mn</td>
<td>16</td>
</tr>
<tr>
<td>2.3.3 Mn in human body</td>
<td>18</td>
</tr>
<tr>
<td>2.4 Fe-Mn alloys as biodegradable materials</td>
<td>19</td>
</tr>
<tr>
<td>2.4.1 Characteristics of Fe-Mn (20–35wt.%Mn) alloys</td>
<td>19</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.4.2 In vitro corrosion of Fe-35wt.%Mn alloys</td>
<td>25</td>
</tr>
<tr>
<td>2.4.3 Biocompatibility of Fe-35wt.%Mn alloys</td>
<td>28</td>
</tr>
<tr>
<td>2.4.4 Summary</td>
<td>29</td>
</tr>
<tr>
<td>2.5 Production of Fe-35wt.%Mn alloys by powder metallurgy</td>
<td>30</td>
</tr>
<tr>
<td>2.5.1 Powder mixing</td>
<td>32</td>
</tr>
<tr>
<td>2.5.2 Powder compaction</td>
<td>37</td>
</tr>
<tr>
<td>2.5.3 Sintering</td>
<td>38</td>
</tr>
<tr>
<td>2.6 Potential biomedical applications of Fe-35wt.%Mn alloys</td>
<td>41</td>
</tr>
<tr>
<td>2.6.1 Coronary artery stenting</td>
<td>41</td>
</tr>
<tr>
<td>2.6.2 Orthopaedics</td>
<td>44</td>
</tr>
<tr>
<td>Chapter 3 Experimental</td>
<td>45</td>
</tr>
<tr>
<td>3.1 Sample preparation</td>
<td>45</td>
</tr>
<tr>
<td>3.1.1 Powder preparation</td>
<td>45</td>
</tr>
<tr>
<td>3.1.2 Die compaction</td>
<td>46</td>
</tr>
<tr>
<td>3.1.3 Debinding</td>
<td>47</td>
</tr>
<tr>
<td>3.1.4 Sintering</td>
<td>47</td>
</tr>
<tr>
<td>3.2 Measurement of density, porosity and open porosity</td>
<td>48</td>
</tr>
<tr>
<td>3.3 Characterization of microstructures</td>
<td>49</td>
</tr>
<tr>
<td>3.4 Corrosion evaluation</td>
<td>49</td>
</tr>
<tr>
<td>3.4.1 Sample preparation</td>
<td>49</td>
</tr>
<tr>
<td>3.4.2 Corrosion media</td>
<td>50</td>
</tr>
</tbody>
</table>
3.4.3 Electrochemical analysis ................................................................. 50

3.4.4 In vitro immersion test................................................................. 51

3.5 Mechanical properties ............................................................................ 53

3.5.1 Hardness testing ............................................................................. 53

3.5.2 Tensile testing ................................................................................ 54

3.5.3 Slow strain rate tensile testing (SSRT) .............................................. 54

3.5.4 Assessment of stress corrosion cracking (SCC) susceptibility ............ 56

3.5.5 Fractography .................................................................................. 56

3.6 Cell compatibility .................................................................................. 56

3.6.1 Extraction preparation ................................................................. 56

3.6.2 Biocompatibility and cell viability .................................................... 57

Chapter 4 Powder Sintering from Blended Elemental (BE) Powder Mixture .......... 59

4.1 Introduction ............................................................................................ 59

4.2 Processing ............................................................................................. 60

4.3 Results and discussion ......................................................................... 61

4.3.1 Density and porosity ...................................................................... 61

4.3.2 Phase constituents and microstructure ............................................ 62

4.3.3 Degradation (corrosion) behavior evaluation ................................... 66

4.3.4 Mechanical properties ................................................................. 72

4.4 Summary ............................................................................................. 76

Chapter 5 Powder Sintering from Mechanically Milled (MMed) Powder ............ 77
5.1 Introduction........................................................................................................... 77

5.2 Processing ............................................................................................................. 78

5.3 Results and discussion ........................................................................................ 80
   5.3.1 Powder preparation by mechanical ball milling ........................................ 80
   5.3.2 Density, porosity, phase constituents and microstructure ....................... 85
   5.3.3 Degradation (corrosion) behavior evaluation ............................................ 89
   5.3.4 Mechanical properties .......................................................................... 103

5.4 Summary ............................................................................................................. 107

Chapter 6 Porous Fe-35wt.%Mn Produced via Sintering from NH₄HCO₃ Porogen........ 109

6.1 Introduction......................................................................................................... 109

6.2 Processing ........................................................................................................... 110
   6.2.1 Powder mixing and compaction............................................................. 110
   6.2.2 Sintering ................................................................................................. 110

6.3 Results and discussion ........................................................................................ 112
   6.3.1 Density and porosity ............................................................................. 112
   6.3.2 Phase constituents and microstructure .................................................. 113
   6.3.3 Degradation (corrosion) behavior evaluation ........................................ 116
   6.3.4 Mechanical properties ........................................................................ 125

6.4 Summary ............................................................................................................. 129

Chapter 7 Stress Corrosion Cracking (SCC) of Fe-35wt.%Mn Alloys ..................... 131

7.1 Introduction......................................................................................................... 131
Co-Authorship Form

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. Please include one copy of this form for each co-authored work. Completed forms should be included in all copies of your thesis submitted for examination and library deposit (including digital deposit), following your thesis Acknowledgements.

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Chapter 5: Powder sintering from mechanically milled powder

Completed reference published journal articles:


<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Experimental design and work, results analysis and report</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent of contribution</td>
<td>83%</td>
</tr>
</tbody>
</table>

**CO-AUTHORS**

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>X. G. Wang</td>
<td>review</td>
</tr>
<tr>
<td>Wei Gao</td>
<td>review</td>
</tr>
<tr>
<td>Peng Cao</td>
<td>review</td>
</tr>
</tbody>
</table>

**Certification by Co-Authors**

The undersigned hereby certify that:
- the above statement correctly reflects the nature and extent of the PhD candidate’s contribution to this work, and the nature of the contribution of each of the co-authors; and
- in cases where the PhD candidate was the lead author of the work, that the candidate wrote the text.

<table>
<thead>
<tr>
<th>Name</th>
<th>Signature</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>X. G. Wang</td>
<td></td>
<td>4/06/2015</td>
</tr>
<tr>
<td>Wei Gao</td>
<td></td>
<td>25/05/2015</td>
</tr>
<tr>
<td>Peng Cao</td>
<td></td>
<td>2/06/2015</td>
</tr>
</tbody>
</table>

Last updated: 23 March 2015
This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. Please include one copy of this form for each co-authored work. Completed forms should be included in all copies of your thesis submitted for examination and library deposit (including digital deposit), following your thesis Acknowledgements.

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

In Chapter 6 Porous Fe-35Mn Produced via Sintering from NH4HCO3 Porogen
Manuscript under review - revision submitting
Title - Degradable Porous Fe-35wt.
Mn Produced via Powder Sintering from NH4HCO3 Porogen
Journal - Materials Chemistry and Physics

<table>
<thead>
<tr>
<th>Nature of contribution by PhD candidate</th>
<th>Experimental design and work, results analysis and report</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent of contribution by PhD candidate (%)</td>
<td>83</td>
</tr>
</tbody>
</table>

### CO-AUTHORS

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peng CAO</td>
<td>Review</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Certification by Co-Authors**

The undersigned hereby certify that:
- the above statement correctly reflects the nature and extent of the PhD candidate’s contribution to this work, and the nature of the contribution of each of the co-authors; and
- in cases where the PhD candidate was the lead author of the work that the candidate wrote the text.

<table>
<thead>
<tr>
<th>Name</th>
<th>Signature</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peng CAO</td>
<td>[Signature]</td>
<td>2/06/2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Last updated: 25 March 2015
Chapter 1 Introduction

1.1 Background

Recent years have seen increasing applications of metallic biomaterials as surgical implants, such as internal bone fixation screws, plates and coronary stents, due to their generally high mechanical strength and good biocompatibility [1]. Historically, much effort has been made to improve the corrosion resistance of the implants, since the corrosion by-products might be allergic and cause biocompatibility concerns. However, a secondary surgical procedure is usually necessary to remove the bone screws and plates if they are made of stainless steel or titanium alloys after the tissue heals [2]. In this regard, the use of a biodegradable implant instead is advantageous over a permanent non-degradable counterpart because a secondary removal is not necessary.

Fe-based alloys group [3-5] is one of the most popular types of biodegradable metals that have been extensively explored in the past decades. Fe is an essential element that is involved in many Fe-containing enzymes and proteins [6, 7]. In recent years, pure iron has been investigated for potential biomedical applications. The \textit{in vivo} animal tests confirm the biocompatibility of Fe - it does not cause significant allergic response or complication if the daily Fe intake is less than 56 mg [8-11]. However, the \textit{in vitro} degradation rate of pure iron is too low and the \textit{in vivo} degradation is even slower than \textit{in vitro} [12]. Another prominent problem for Fe arises from its ferromagnetic nature, causing the Fe materials incompatible with magnetic resonance imaging (MRI) [13]. Alloying Fe by Mn provides a solution to the MRI problems [5]. When Mn is over 29wt.%, the quenched Fe-Mn alloys exhibit a completely austenitic $\gamma$ phase that is non-magnetic [14]. In 2008, Hermawan \textit{et al.} proposed a composition of Fe-35wt.%Mn [3]. The alloy demonstrates good mechanical properties, non-toxicity and non-magnetization [3, 13, 15].

In a previous study [3], a dense Fe-35Mn alloy was produced via powder metallurgical (PM) routes, followed by cold rolling. The alloy demonstrated satisfactory tensile properties (yield strength, tensile strength and elongation) compared with stainless steel. It degraded approximately three times faster than pure iron [15]. However it was considered still slow by comparing with the optimum degradation period of after 6~12 months implantation. To further increase the degradation rate, PM technique was employed in
current work as literature but not followed with any post-treatment. A simple blend-press-sinter method was adopted, and three types of starting powder including blended elemental (BE), mechanically milled (MMed) Fe-Mn powder and BE powder with spacing holding materials were prepared for producing Fe-35Mn alloys, aiming to obtain less dense even porous Fe-35Mn alloys with high porosity level in order to approach the expecting corrosion rate. Therefore, the process of preparing starting powder and the characterizations of final sintered Fe-35Mn alloys were investigated in this doctoral thesis.

1.2 Objectives

The objective of this research project is to produce less dense Fe-35Mn alloys by a PM method to be as potential biodegradable materials. Fabrication of Fe-35Mn alloys via a PM route is aiming at obtaining alloys with higher porosity, higher corrosion rate and moderate mechanical properties compared to those previously researched dense Fe-35Mn alloys. A stress corrosion cracking (SCC) experiment and a biocompatibility investigation will be also performed to prove their viability for bio-medical applications. The approaches are described in details as follows.

(i) To investigate the effects of sintering parameters including temperature and holding time on the sintered density, microstructure, mechanical properties and \textit{in vitro} corrosion behaviors of the sintered samples.

(ii) To develop a mechanical milling (MMing) technique to produce fine-grained Fe-Mn alloys that have highly improved mechanical properties and establish the relationship between processing parameters, microstructure, mechanical properties and \textit{in vitro} corrosion behavior.

(iii) To develop a space holding technique to fabricate porous Fe-35Mn alloys with much higher corrosion rate and investigate the microstructure and other properties.

(iv) To establish a SCC assessment on produced Fe-35Mn alloys.

(v) To evaluate the \textit{in vitro} biocompatibility of the sintered samples.
1.3 Thesis outline

This thesis consists of 9 chapters, and part of the presented results has been published by the author of this thesis [16]. The detailed framework of current thesis is listed below:

Chapter 1 introduces the field of current degradable Fe-35Mn alloys, the idea behind this doctoral study, and objectives of the study. It also covers the outlines of the entire thesis.

Chapter 2 is a literature study section of this thesis. It presents an extensive literature survey and critics on the development from biomaterials to metallic degradable biomaterials, then to iron based biometals, finally to Fe-35Mn alloys. The literature review also provides an overview of the processing techniques for making Fe-35Mn alloys by PM and the potential applications of the novel Fe-35Mn alloys.

Chapter 3 describes the experimental process of producing Fe-35Mn alloys and materials analysis including porosity measurements, microstructure observation, corrosion behavior investigation, tensile testing, fractography, SCC measurement and biocompatibility evaluation.

Chapters 4, 5 and 6 present the results of Fe-35Mn alloys produced by three types of powder. They are BE powder, MMed powder and BE powder with space holding material, respectively. Porosity measurements, microstructure observation, corrosion behavior, tensile testing and fractography are reported in these three chapters.

Chapter 7 mainly focuses on SCC. A slow strain rate testing (SSRT) was conducted in corrosive environment under different strain rates.

Chapter 8 reports the biocompatibility of the new Fe-Mn alloys by a resazurin fluorescence assay on murine fibroblast cell line L929. The cell proliferation investigation and cell morphology observation are performed.

Chapter 9 concludes the main findings of the doctoral works and suggests some future works for the continuation of this doctoral study.
Chapter 2 Literature Review

2.1 Biomaterials

The broad term ‘biomaterials’ refers to [17]:

(i) Synthetic materials used to replace part of a living system or to function in intimate contact with living tissue.
(ii) A systemically and pharmacologically inert substance which designed for implantation within or incorporation with living systems.
(iii) A nonviable material used in a medical device intended to interact with biological systems.
(iv) Materials of synthetic as well as natural origin in contact with tissue, blood, and biological fluids and intended for use for prosthetic, diagnostic, therapeutic, and storage applications without adversely affect the living organism and its components.
(v) Substance (other than drugs) or combinations of substances synthetic or natural in origin which can be used for any period of time, as a whole or part of a system, which treats, augments, or replaces any tissue organ or function of the body.

At the early stages of development, biomedical materials are synthetic materials, such as metals, polymers and ceramics. In recent years, natural materials have accounted for a significant usage of biomaterials, one example of which being the hybrid material that combines living cells and non-living materials. Nowadays, almost all human organs except brain have artificial substitutes, which are manufactured from biomaterials. The increasing expectations for a higher quality of healthy life have required the development of new technologies for better implants with higher clinical performance and the development of new biomaterials is one of most demanding scientific challenges.

In terms of the chemical compositions, biomaterials can be classified into biomedical metals and alloys (biometals), biomedical polymeric materials (biopolymers), biomedical ceramics (bioceramics), and the combination of these three to make biomedical composites (biocomposites). Table 2.1 lists some important biomaterials, their properties and applications [17].
Biomaterials are often used (and/or adapted) for a medical application. Biomaterials should comprise the whole or a part of a living structure or biomedical device which performs, augments, or replaces a natural function. In general, biomaterials are usually used in bone cement, joint replacements, contact lenses, breast implant, dental implants for tooth fixation, skin repair devices (artificial tissue), coronary stents, bone plates, artificial ligaments and tendons, blood vessel prostheses, heart valves and cochlear replacements.
Table 2.1 - Typical biomedical materials and properties [17].

<table>
<thead>
<tr>
<th>Material</th>
<th>Strength</th>
<th>Elastic modulus</th>
<th>Fatigue Life</th>
<th>Biostability</th>
<th>Bioactivity</th>
<th>Sterilizability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylics</td>
<td>Mod</td>
<td>Mod</td>
<td>Mod</td>
<td>High</td>
<td>Low</td>
<td>E/R</td>
</tr>
<tr>
<td>Poly(carbonates)</td>
<td>Mod</td>
<td>Mod</td>
<td>Mod</td>
<td>High</td>
<td>Low</td>
<td>E/R/H</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>E/R</td>
</tr>
<tr>
<td>Silicones</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>E/R/H</td>
</tr>
<tr>
<td>Poly(amino acids)</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>B</td>
<td>Mod/High</td>
<td>E/R</td>
</tr>
<tr>
<td>Poly(lactic/glycolic)</td>
<td>Mod</td>
<td>Low</td>
<td>Mod</td>
<td>B</td>
<td>Low</td>
<td>E/R</td>
</tr>
<tr>
<td>acid copolymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(anhydrides)</td>
<td>Mod</td>
<td>Low</td>
<td>Mod</td>
<td>S</td>
<td>Low</td>
<td>E/R</td>
</tr>
<tr>
<td>Metals and alloys</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-Cr alloys</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>H/E/R</td>
</tr>
<tr>
<td>Ni-Cr alloys</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>H/E/R</td>
</tr>
<tr>
<td>Nitinol(Ni-Ti) alloys</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>H/E/R</td>
</tr>
<tr>
<td>Material Type</td>
<td>Biostability</td>
<td>Bioactivity</td>
<td>Sterilizability</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------------</td>
<td>-------------</td>
<td>-----------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Stainless steel</strong></td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tantalum</strong></td>
<td>High</td>
<td>High</td>
<td>Mod</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Titanium &amp; its alloys</strong></td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ceramics: inorganics and glasses</strong></td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>alumina</strong></td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Porous alumina</strong></td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Composites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Epoxy</strong></td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Poly(olefins)</strong></td>
<td>Low</td>
<td>Low</td>
<td>Mod</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All properties are classified as low (Low), moderate (Mod), or high (High), except as noted in the text and below.

1. **Biostability**: This term refers to the material’s long-term stability in a biologic environment [17-20]. C = Calcitic deposits leading to degradation of properties. Materials that are used for their bioreabsorability are noted by the manner in which they resorb as follows [17]: B = bulk biodegradable; S = surface biodegradable.

2. **Bioactivity**: This term refers to properties that relate to increasing cell adhesion, actively controlling blood enzyme interactions, or antimicrobial activity.

3. **Sterilizability**: Some of the following processes, e.g., radiation, can change biostability or biodegradation rates, depending on whether bonds are broken or new cross-links induced. H = heat; E = ethylene oxide; R = gamma radiation or electron beam; C = aqueous chemical, e.g., aldehyde or propylene oxide; F = sterile filtration.
2.2 Biodegradable materials

In recent years, a paradigm shift has been evidenced. A material’s corrodbility is elaborately used to develop biodegradable materials. The concept of degradable biomaterials was proposed in 1988 [21]. The term “biodegradable” typically refers to materials in which active biological processes are involved.

Increasing applications of biodegradable materials as a surgical implant or stent have been seen nowadays [6]. The benefit of using biodegradable materials in human body is apparent. They can adapt to the human body in which they are implanted and then gradually degrade till eventually dissolve after the healing process. Consequently patients would no longer suffer from a secondary surgery to remove the previously implanted devices. Commonly used and widely developed biodegradable materials are biodegradable polymers and metals. They are further discussed in the following sections.

2.2.1 Biodegradable polymers

Biodegradable polymer is the most commonly known biodegradable material. These materials have been extensively investigated for many decades since their introduction in the late 1980s. The applications of biodegradable polymers have been focused on three major areas; medical [22, 23], agricultural [24, 25], and consumer goods packaging [25, 26]. Medical applications are the most popular amongst these three application areas.

Biopolymers include synthetic polymers and nature (bioderived) polymers. Synthetic biopolymers are the ones commonly used. They can be customer-produced and designed to eliminate the drawbacks of natural polymers and add some preferable features (such as controllable corrosion behavior and certain bioactivity, etc.). Typical biosynthetic polymers include poly-lactic acid (PLA) [27], poly-L-lactic-acid (PLLA) [6, 28], polyglycolic acid and polycaprolactone [29-35]. In comparison to other materials, the major drawbacks of degradable polymers include low mechanical strength and too low modulus of elasticity [34]. Devices such as stents, made of these polymers, have shown high incident of recoil because of low Young’s modulus. For load-bearing applications, metals with a much higher strength while good ductility are still the primary choice of biomaterials.
2.2.2 Biodegradable metals

The application of using metals in medical field has a long history. Metals are the first generation of biomaterials. Metals, in general with favorable combination of tensile strength, fracture toughness and fatigue strength, warrant their application in orthopaedics than polymers and therefore are more suitable for load-bearing implants. Table 2.2 also lists some typical characteristics of metals, in comparison with polymers and ceramics.

Apart from some permanent biometals, such as stainless steel grade 316L (SS316L) [36, 37], titanium and its alloys [38, 39], nickel-titanium shape memory alloys [40-43], cobalt-chromium alloys [44, 45] and noble metal alloys [39, 46], Mg-based [47-52] and Fe-based alloys [3-5, 12, 13, 53, 54] are the two classes of widely researched biodegradable metals [55]. Experiments on animals [8-10, 49, 56-58] and clinical trials [59-62] have proved the feasibility of biodegradable metals as safe implanting materials.
Table 2.2 - Comparison of various biomaterials [17, 63, 64].

<table>
<thead>
<tr>
<th>Material properties</th>
<th>Metal</th>
<th>Polymers</th>
<th>Ceramics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biocompatibility</td>
<td>Some are not very good</td>
<td>Excellent</td>
<td>Good</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>most metals are not corrosion resistant</td>
<td>Stable chemical properties, corrosion resistant</td>
<td>Stable chemical properties, corrosion resistant, hardly get oxidized, hydrolyzed and degraded</td>
</tr>
<tr>
<td></td>
<td>(exclude Ti and noble metals)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat resistance</td>
<td>Fine for thermal shock</td>
<td>Easily get heat deformation and aging</td>
<td>Good for thermal shock</td>
</tr>
<tr>
<td>Strength</td>
<td>Very high</td>
<td>Low</td>
<td>High under compression</td>
</tr>
<tr>
<td>Wear resistance</td>
<td>Not very good, wear products would contaminate surrounding tissue</td>
<td>Bad</td>
<td>Good</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>High</td>
<td>Low</td>
<td>Very high</td>
</tr>
<tr>
<td>Toughness</td>
<td>High</td>
<td>Most of them are high</td>
<td>Low</td>
</tr>
<tr>
<td>Machining molding performance</td>
<td>Good. Easy to be machined into any shape.</td>
<td>Fine</td>
<td>Bad</td>
</tr>
</tbody>
</table>
2.2.3 Biodegradable Mg and Mg alloys

Magnesium has been considered safe to be used as implantable materials [65]. The first production of metallic magnesium was made by Sir Humphry Davy in 1808 [52, 66]. At present, magnesium and its alloys are popular in their applications as cardiovascular or orthopaedic devices [46, 67] and magnesium metal stents (e.g. AMS, BiotronikGmBH) have been moved to clinical arena since 2006 [14]. Two magnesium-based alloys are also reported for making stents currently: AE21 (Mg-2%Al-1% rare earth) [48, 68, 69] and WE43 (Mg-4%Y-3.3% rare earth) [37, 70]. Biocompatibility performances of these alloys are investigated to be similar to that of iron, as magnesium is present naturally in the human body as well.

These Mg alloys, however, may fracture under relatively low loading (listed in Table 2.3) due to their poor strength. Also because of its resistance to radiant energy, it cannot be imaged by X-rays. Poor mechanical properties compared with 316L stainless steel, fast degradation rate [49, 52, 56, 71-74] (the standard electrode potential of pure Mg is -2.37 V [69]) in vivo and significant hydrogen evolution during the corrosion process significantly limit their future bioapplications. Therefore, for biodegradable Mg alloys, their corrosion resistance needs to be further enhanced. The approaches include alloying [75], coating such as with dicalcium phosphate dehydrate (DCPD) [76] and surface modification by such as alkali heat treatment [6].

Table 2.3 - Summary of the physical and mechanical properties of typical metallic implant materials [52].

<table>
<thead>
<tr>
<th>Implanted Material</th>
<th>Density g/cm³</th>
<th>Elastic modulus GPa</th>
<th>Compressive strength MPa</th>
<th>Fracture Toughness MPa·√m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>1.74~1.90</td>
<td>41~45</td>
<td>65~100</td>
<td>~15</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>4.4~4.5</td>
<td>110~117</td>
<td>758~1117</td>
<td>60</td>
</tr>
<tr>
<td>Co-Cr alloys</td>
<td>8.3~9.2</td>
<td>230</td>
<td>450~1000</td>
<td>--</td>
</tr>
<tr>
<td>Stainless steels</td>
<td>7.9~8.1</td>
<td>189~205</td>
<td>170~310</td>
<td>~100</td>
</tr>
</tbody>
</table>
2.3 Biodegradable iron and its alloys

Iron is an element that is naturally present in many foods (such as oysters, tofu, nuts, chocolate and spinach, etc. [77]). Iron is also an essential element for most living organisms and it plays important roles in the human body. Because it is a crucial component of enzymes and proteins [6, 78], iron is related to the internal transport, storage and activation of molecular oxygen, and the reduction of ribonucleotides and dinitrogen [7].

The recommended intake for iron and other nutrients are provided in the Dietary Reference Intakes (DRIs) developed by the Food and Nutrition Board (FNB) at the Institute of Medicine (IOM) of the National Academies [79]. Recommended Dietary Allowance (RDA) is the average daily level of intake sufficient to meet the nutrient requirements of nearly all (97%–98%) healthy individuals. Tolerable Upper Intake Level (UL): is the maximum daily intake unlikely to cause adverse health effects. Table 2.4 lists the current iron RDAs and ULs for each people group.

Table 2.4 - Recommended daily intake and upper limit of iron [79, 80]

<table>
<thead>
<tr>
<th></th>
<th>Iron mg per day</th>
<th>Upper limit mg per day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birth to 6 months</td>
<td>0.27</td>
<td>40</td>
</tr>
<tr>
<td>Infants (7~12 months)</td>
<td>11</td>
<td>40</td>
</tr>
<tr>
<td>Children (1~13 years)</td>
<td>7.10</td>
<td>40</td>
</tr>
<tr>
<td>Boys (14~18 years)</td>
<td>11</td>
<td>45</td>
</tr>
<tr>
<td>Girls (14~18 years)</td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td>Women (19~50 years)</td>
<td>18</td>
<td>45</td>
</tr>
<tr>
<td>Pregnant women</td>
<td>27</td>
<td>45</td>
</tr>
<tr>
<td>Breastfeeding women</td>
<td>9~10</td>
<td>45</td>
</tr>
<tr>
<td>Women over 50 years</td>
<td>8</td>
<td>45</td>
</tr>
<tr>
<td>Men over 19 years</td>
<td>8</td>
<td>45</td>
</tr>
</tbody>
</table>
2.3.1 Pure iron

In recent years, pure iron as a biodegradable material has been investigated. The mechanical properties of pure Fe are close to those of SS316L and superior than Mg alloys, as shown in Table 2.5. In the design of endovascular devices such as stents, tensile strength is an important property. Iron has superior radial strength which offers a dominant factor for iron as a scaffolding biomedical material. Degradation products of iron and its alloys also form ferrous and ferric ions, which can dissolve into the biological medium. The presence of ferrous ions discourages proliferation of smooth muscle cells in the blood vessels, therefore indicating that it may inhibit neointimal hyperplasia. Nevertheless, recent results of ‘in vivo’ animal tests [8-10] showed iron is a biocompatible metal without significant obstruction of the stented vessel due to inflammation, neointimal proliferation, or thrombotic events [81]. However there are some issues associated with iron that needs to be addressed:

(vi) Degradation rate of pure iron is still too slow.
(vii) In vivo experiments show that the degradation performance is not as satisfactory as in in-vitro experiments [12].
(viii) The ferromagnetic nature of iron is not compatible with MRI facility [82].

The main limitation with pure iron is its slow degradation rate, which leads to a development of fast degradable Fe-based alloys. As proposed by Schinhammer et al. [5], the design strategy for Fe-based alloys should focus on both an improvement in the mechanical properties and an increase in the degradation rate, by developing new alloy chemistry and optimizing the microstructures. Alloying iron is also one approach to solve the ferromagnetic problem [83].
Table 2.5 - Properties of degradable iron implanted compared with those of SS316L and Mg [14].

<table>
<thead>
<tr>
<th></th>
<th>SS316L annealed plate</th>
<th>Iron annealed plate</th>
<th>WE43 Magnesium alloy T6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition (wt.%)</strong></td>
<td>Fe, 16–18.5Cr, 10–14Ni, 2–3Mo, &lt;2Mn, &lt;1Si, &lt;0.03C</td>
<td>99.8 Fe</td>
<td>Mg, 3.7–4.3Y, 2.4–4.4Nd, 0.4–1Zr</td>
</tr>
<tr>
<td><strong>Density (g/cm³)</strong></td>
<td>8.00</td>
<td>7.87</td>
<td>1.84</td>
</tr>
<tr>
<td><strong>Ferromagnetic/non-ferromagnetic</strong></td>
<td>Non-ferromagnetic</td>
<td>Ferromagnetic</td>
<td>Non-ferromagnetic</td>
</tr>
<tr>
<td><strong>Yield strength (MPa)</strong></td>
<td>190</td>
<td>150</td>
<td>170</td>
</tr>
<tr>
<td><strong>Tensile strength (MPa)</strong></td>
<td>490</td>
<td>210</td>
<td>220</td>
</tr>
<tr>
<td><strong>Young’s modulus (GPa)</strong></td>
<td>193</td>
<td>200</td>
<td>44</td>
</tr>
<tr>
<td><strong>Elongation (%)</strong></td>
<td>40</td>
<td>40</td>
<td>2</td>
</tr>
</tbody>
</table>
2.3.2 Alloy development by incorporating Mn

In order to develop an alloy with higher degradation rate, alloying with other elements is a common approach. The new alloys also have to be compatible with MRI imaging. It is widely known that C, Mn, P, Si, S, B, Ni, Cr, Mo, Pb, Al, Cu, Ti, Co, V, and W are common alloying elements in industrial steels. Therefore, the alloying iron approach starts from these elements. Owing to the fact that alloying iron with Cr, Ni, Mo, Cu, Ti, V, and Si would improve the corrosion resistance and Pb is both nephrotoxic and toxic to the hematopoietic and nervous systems [84], these elements are eliminated to be as alloying iron candidates. Liu et al. [81] developed a series of Fe-3 at.%X binary alloys, where X = Mn, Co, Al, W, Sn, C, or B. The addition of elements Co, W, and C to iron had improved the mechanical properties and biocompatibility and all the Fe-3X binary alloy degradation rates were close to that of pure iron (shown in Table 2.6). As a result, Mn, Co, Al, W, B, C and S are all potential candidates for alloying iron. But two aspects are still needed to be ameliorated. Firstly, little amount addition of alloying element remains iron in a ferro-magnetic α phase which would affect the MRI examination in clinic. Secondly, the degradation rates are still slow. Researchers predicted that the increase in alloying element content can transfer from α-iron to another phase which would alter the ferro-magnetic property of α-iron and it also might be useful to accelerate the degradation rate of Fe-based alloys. Therefore, a higher alloying element content is highly in demand.

Hermawan et al. [3, 15, 85] developed a series of Fe-Mn alloys with Mn content between 20 and 35 weight percent. Results showed that γ-austenite was the main phase with the appearance of ε-martensite phase in Fe-Mn alloys with lower Mn content (20~25%Mn). In addition, corrosion rates were proofed to be significantly higher than those of pure iron. Comparable mechanical properties with 316SSL and low inhibition of fibroblast cell metabolic activity in cell viability tests were also achieved. At present, a considerable breakthrough has been made on the research of biodegradable iron-manganese alloys (with high content of Mn >20wt.%) showing that alloying pure iron by high content Mn is feasible, where the limitations (e.g. slow degradation rate and MRI incompatibility) of pure iron as a biodegradable material can be complemented. More studied achievements on Fe-(20~35wt.%)Mn alloys will be demonstrated in section 2.5.
Table 2.6 - Electrochemical data of Fe-3 at.%X (X = Mn, Co, Al, W, B, C and S) binary alloys as compared with pure iron [81].

<table>
<thead>
<tr>
<th></th>
<th>Vcorr (V)</th>
<th>Icorr (μA cm⁻²)</th>
<th>Corrosion rate (g m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure iron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-cast</td>
<td>-0.748</td>
<td>8.961</td>
<td>2.240</td>
</tr>
<tr>
<td>As-rolled</td>
<td>-0.702</td>
<td>8.768</td>
<td>2.192</td>
</tr>
<tr>
<td>Fe-3at.%Mn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-cast</td>
<td>-0.711</td>
<td>9.003</td>
<td>2.251</td>
</tr>
<tr>
<td>As-rolled</td>
<td>-0.68</td>
<td>7.454</td>
<td>1.861</td>
</tr>
<tr>
<td>Fe-3at.%Co</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-cast</td>
<td>-0.713</td>
<td>10.966</td>
<td>2.741</td>
</tr>
<tr>
<td>As-rolled</td>
<td>-0.693</td>
<td>12.099</td>
<td>3.025</td>
</tr>
<tr>
<td>Fe-3at.%Al</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-cast</td>
<td>-0.704</td>
<td>9.538</td>
<td>2.385</td>
</tr>
<tr>
<td>As-rolled</td>
<td>-0.721</td>
<td>9.485</td>
<td>2.372</td>
</tr>
<tr>
<td>Fe-3at.%W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-cast</td>
<td>-0.717</td>
<td>12.89</td>
<td>3.223</td>
</tr>
<tr>
<td>As-rolled</td>
<td>-0.709</td>
<td>12.663</td>
<td>3.166</td>
</tr>
<tr>
<td>Fe-3at.%B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-cast</td>
<td>-0.698</td>
<td>14.962</td>
<td>3.741</td>
</tr>
<tr>
<td>As-rolled</td>
<td>-0.728</td>
<td>10.309</td>
<td>2.577</td>
</tr>
<tr>
<td>Fe-3at.%C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-rolled</td>
<td>-0.68</td>
<td>15.954</td>
<td>3.991</td>
</tr>
<tr>
<td>Fe-3at.%S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-rolled</td>
<td>-0.703</td>
<td>0.145</td>
<td>3.088</td>
</tr>
</tbody>
</table>

*Vcorr, corrosion potential; Icorr and corrosion current density.
2.3.3 Mn in human body

There is approximately 10~20 mg of manganese in the human body. Most of Mn element exists in the liver, kidneys and bones [86]. Manganese (II) ions function as cofactors for a large variety of enzymes, including mitochondrial superoxide dismutase, phosphoglucomutase, pyruvate cholinesterase, carboxylase, and several phosphates, peptidases and glycosyltransferases [87]. Hence, a certain amount of Mn ions release to human body from the biodegradable Fe-Mn alloys is considered safe, considering Mn is a requisite element to human. However, excess manganese interferes with the absorption of dietary iron. Long-term exposure to excess levels may result in iron-deficiency anemia. Increased manganese intake also impairs the activity of copper metallo-enzymes. The RDA and UL of manganese daily intake are shown in Table 2.7. These values are some important consideration factors when people design the degradation rate of Fe-Mn alloys.

Table 2.7 - Recommended dietary manganese intake and upper limit [80].

<table>
<thead>
<tr>
<th>Age by years</th>
<th>Manganese mg per day</th>
<th>Upper limit mg per day</th>
</tr>
</thead>
<tbody>
<tr>
<td>1~3</td>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>4~8</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>9~13 (male)</td>
<td>1.9</td>
<td>6</td>
</tr>
<tr>
<td>9~13 (female)</td>
<td>1.6</td>
<td>6</td>
</tr>
<tr>
<td>14~18 (male)</td>
<td>2.2</td>
<td>9</td>
</tr>
<tr>
<td>14~18 (female)</td>
<td>1.6</td>
<td>9</td>
</tr>
<tr>
<td>Adult male</td>
<td>2.3</td>
<td>11</td>
</tr>
<tr>
<td>Adult female</td>
<td>1.8</td>
<td>11</td>
</tr>
<tr>
<td>Pregnant female</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>Breast feeding female</td>
<td>2.6</td>
<td>11</td>
</tr>
</tbody>
</table>
2.4 Fe-Mn alloys as biodegradable materials

2.4.1 Characteristics of Fe-Mn (20~35wt.%Mn) alloys

The first attempt to design the compositions of the high Mn content Fe-Mn binary alloys was carried out by Hermawan and his colleagues in 2008 [3, 85]. A series of Fe-Mn alloys with the Mn content between 20wt.% and 35wt.% were developed via powder metallurgy (PM) route, followed by cold rolling and quenching. The main design objective of their study was to change the ferro-magnetic nature of iron by adding a high content of Mn.

![Figure 2.1 - Volume fraction of constituent phase in cast Fe-Mn alloys with the concentration of manganese in the alloy, from Hermawan et al.[15].](image)

As indicated in Fig. 2.1, the ε and γ are the main phases when Mn addition is beyond 20wt.%, while manganese of > 29wt.%, single γ becomes the dominant phase. It has been known that ε and γ phases, which are martensitic and austenitic respectively, have antiferromagnetic properties [88, 89]. Thus, Fe-Mn alloys containing exclusively these
phases are nonmagnetic. The microstructures of Fe-Mn alloys with different Mn contents are shown in Fig. 2.2. The presence of lamellar microstructure of dual $\gamma + \varepsilon$ phases was observed in the Fe-20Mn and Fe-25Mn alloys (Figs. 2.2 (a) and 2.2 (b)), whereas single $\gamma$ phase was observed in Fe-30Mn and Fe-35Mn (Figs. 2.2 (c) and 2.3 (d)). To further explain this phenomenon, Jun and Choi [90] studied the influence of Mn content on microstructure and damping capacity in Fe-(17-23)Mn alloys. They concluded that the amount of $\varepsilon$ martensite decreased simultaneously with increasing Mn content [90]. Both $\gamma$ and $\varepsilon$ phases are antiferromagnetic and therefore the Fe-(>17)Mn alloys are MRI compatible [91]. The magnetic susceptibility shown in Fig. 2.3 and the magnetization curves shown in Fig. 2.4 of Fe-(20–35)Mn alloys consistently verified their anti-ferromagnetic nature and reveal the MRI compatibility. All the Fe-Mn alloys studied presented superior magnetic compatibility than stainless steel SS316L.

Figure 2.2 - Microstructure of (a) Fe-20Mn, (b) Fe-25Mn, (c) Fe-30Mn and (d) Fe-35Mn after sintering and quenching, respectively, from Hermawan et al. [15].
Figure 2.3 - Magnetic susceptibility of Fe-Mn specimens after quenching and after cold rolling, from Hermawan et al. [15].

Figure 2.4 - Magnetization curves of sintered and quenched Fe-Mn specimens compared with that of annealed SS316L alloy, from Hermawan et al. [15].
Nevertheless, from a microstructural point of view, the presence of different phases in the alloy would also affect the mechanical and corrosion properties. Based on the study by Hermawan et al. [15], the dual phase (\(\gamma\) and \(\varepsilon\)) alloys (e.g., Fe-20Mn and Fe-25Mn) had higher strength but were less ductile than the single \(\gamma\)-phase alloy (Fe-30Mn and Fe-35Mn). Fig. 2.5 illustrates the typical stress strain curves of the Fe-Mn alloys containing 20, 25, 30, and 35 wt% Mn. The mechanical properties of those Fe-Mn alloys shown in Table 2.8 indicated that the increase in Mn content resulted in a lower ultimate tensile strength (UTS) and a larger elongation. This is because of the harder and denser \(\varepsilon\) phase and the larger grains of \(\gamma\) phase. Considering the overall mechanical properties, Fe-30Mn and Fe-35Mn were comparable with SS316L, indicated in Table 2.8. They met the minimum requirement of ASTM F138 for stainless steel 316L.

![Figure 2.5 - Typical stress strain curves of Fe-Mn specimens containing 20, 25, 30, and 35 wt% Mn, from Hermawan et al. [15].](image)
In addition to the satisfactory mechanical properties [15], these Fe-Mn alloys have shown desired corrosion rate compared with annealed pure iron, AM60b-F Mg alloy and 316SSL. These Fe-Mn alloys corroded faster than pure iron and 316SSL but significantly slower than Mg alloys. As shown in Fig. 2.6 and Table 2.9, the addition of Mn accelerated the corrosion of pure iron. In general, in the range between 20~35 weight percent of alloying Mn, a higher Mn content leads to a slightly lower corrosion rate. Moreover, the corrosion rate of dual $\gamma + \varepsilon$ phase alloys was higher than the single $\gamma$ phase alloys. The presence of dual phases in the Fe-Mn alloy would increase the number of micro-galvanic sites for corrosion, which in turn made the degradation faster than the single $\gamma$ phase alloy [15].

Considering mechanical properties, magnetic susceptibility and corrosion behavior, Fe-Mn alloys with >30wt% Mn has become the best choice for biomedical applications. Therefore, the compositions of Fe-35wt.%Mn are selected in this study.

Table 2.8 - Mechanical properties of Fe-Mn alloys [15]

<table>
<thead>
<tr>
<th>Materials</th>
<th>UTS (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Elongation at Break (%)</th>
<th>Hardness HRA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-20Mn</td>
<td>702 (11)</td>
<td>421 (27)</td>
<td>7.5 (1.5)</td>
<td>59 (1)</td>
</tr>
<tr>
<td>Fe-25Mn</td>
<td>723 (19)</td>
<td>316 (33)</td>
<td>4.8 (0.4)</td>
<td>56 (1)</td>
</tr>
<tr>
<td>Fe-30Mn</td>
<td>518 (14)</td>
<td>239 (13)</td>
<td>19.0 (1.4)</td>
<td>40 (1)</td>
</tr>
<tr>
<td>Fe-35Mn</td>
<td>428 (7)</td>
<td>234 (7)</td>
<td>32.0 (0.8)</td>
<td>38 (2)</td>
</tr>
<tr>
<td>316 SSL</td>
<td>490</td>
<td>190</td>
<td>40.0</td>
<td>/</td>
</tr>
</tbody>
</table>
Figure 2.6 - Polarization curves of quenched Fe-Mn specimens containing 20, 25, 30 and 35 wt% Mn in comparison with pure iron, from Hermawan et al. [15].

Table 2.9 - Corrosion Rate of quenched Fe-Mn Alloys in comparison to pure iron annealed, AM60B Mg alloy and 316L [15, 54]

<table>
<thead>
<tr>
<th>Material</th>
<th>I_{corr} (μA/cm²)</th>
<th>CR (mmpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-20Mn</td>
<td>113(4)</td>
<td>1.3(0.1)</td>
</tr>
<tr>
<td>Fe-25Mn</td>
<td>91(4)</td>
<td>1.1(0.1)</td>
</tr>
<tr>
<td>Fe-30Mn</td>
<td>56(5)</td>
<td>0.7(0.1)</td>
</tr>
<tr>
<td>Fe-35Mn</td>
<td>37(3)</td>
<td>0.4(0.1)</td>
</tr>
<tr>
<td>316 SSL</td>
<td>16(2)</td>
<td>0.2(0.1)</td>
</tr>
<tr>
<td>Pure iron, annealed</td>
<td>14(4)</td>
<td>0.2(0.1)</td>
</tr>
<tr>
<td>AM60B Mg alloy</td>
<td>406</td>
<td>2.8</td>
</tr>
</tbody>
</table>

*I_{corr} - corrosion current density; CR - corrosion rate; mmpy – mm per year.*
2.4.2 *In vitro* corrosion of Fe-35wt.%Mn alloys

In 2010, Hermawan *et al.* [13] investigated the degradation behavior of Fe-35Mn alloy in Hank’s solution for 3 months. A specific test bench (illustrated in Fig. 2.7) was used to investigate the degradation in flow conditions that mimic those of coronary artery. The test is termed ‘dynamic immersion’. The SEM images of the Fe-35Mn surface after 3 months’ degradation are shown in Fig. 2.8. After 3 months dynamic immersion, the Fe-35Mn alloys corroded severely. The degradation products adhered to the metal surface and were not completely washed out by the flowing solution in the test bench. The surface was covered by a flat degradation product layer and spreading agglomerates formed on it. As detected by EDX, XRD and XPS on the corrode surface, the degradation products contained iron and manganese oxides, hydroxides and calcium/phosphorus.

![Schematic view of a dynamic immersion test bench](image)

Figure 2.7 - Schematic view of a dynamic immersion test bench and close-up upside view of the test channel with specimen in place. Note: Le= length of laminar flow between the specimen and chamber, W= width and H= height of the test channel, from Levesque *et al.*[92].
A degradation mechanism of the Fe-Mn alloy during the dynamic immersion test in modified Hank’s solution was proposed, which could be divided into four steps as follows. The schematic diagram of the mechanism is illustrated in Fig. 2.9.

Step 1. Initial corrosion reaction (Fig. 2.9 (a))

When the Fe-Mn alloy is in contact with the test solution, the alloy is oxidized into metal ions following the anodic reaction as shown in Eqs. 2.1 and 2.2. The electrons that have been generated from the reaction are consumed by the cathodic reaction corresponding to the reduction of oxygen dissolved in water, as shown in Eq. 2.3.

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \\
\text{Mn} & \rightarrow \text{Mn}^{2+} + 2e^- 
\end{align*}
\]  

(Eq. 2.1)  

(Eq. 2.2)
Chapter 2 Literature Review

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ \hspace{1cm} (Eq. 2.3)

These reactions occur randomly over the entire surface where a difference in potential exists at the grain boundaries and at the interface between different phases.

2. Formation of hydroxide layers (Fig. 2.9 (b))

The metal ions released from the initiation corrosion reactions react with the hydroxyl ion ($OH^-$) released from the cathodic reaction (Eq. 2.3) to form insoluble hydroxides (hydrinous metal oxides) shown in Eqs 2.4 and 2.5. The equations are written for iron only because it is the main composition of the alloy.

\[ 2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2 \text{ or } 2FeO \cdot 2H_2O \] \hspace{1cm} (Eq. 2.4)

\[ 4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \text{ or } 2Fe_2O_3 \cdot 6H_2O \] \hspace{1cm} (Eq. 2.5)

After this step, the iron alloy will normally have 3 different layers. FeO·nH$_2$O is at the bottom, Fe$_3$O$_4$·nH$_2$O in the middle and Fe$_2$O$_3$·nH$_2$O on the top [93].

3. Formation of pits (Fig. 2.9 (c))

Since the hydroxide layers did not homogenously cover the surface, Cl$^-$ ions from the solution have penetrated to compensate the increase of metal ions beneath the hydroxide layer. The formed metal chloride is then hydrolysed by water to the hydroxide and free acid, Eq. 2.6, lowering the pH value in the pits while the bulk solution remains neutral.

\[ Fe^{2+} + 2Cl^- \rightarrow FeCl_2 + H_2O \rightarrow Fe(OH)_2 + HCl \] \hspace{1cm} (Eq. 2.6)

4. Formation of calcium/phosphorus layer (Fig. 2.9 (d))

As the degradation process continues, the formation of a new layer containing with calcium and phosphorus occurs. Interestingly, these two elements can lead to the formation of hydroxyapatite when they are at the right ratio. Hydroxyapatite is considered to be biocompatible for bone implants.
2.4.3 Biocompatibility of Fe-35wt.%Mn alloys

The cell viability on the Fe-35Mn alloys was investigated using fibroblast cells by a water soluble tetrazolium essay [13]. It is found that the Fe-Mn alloys possessed a low inhibition effect to 3T3 fibroblast cells metabolic activities compared to pure manganese (shown in Fig. 2.10) due to the effect of alloying. At low alloy concentrations in cellular medium, the inhibition effect is negligible, in other words, Fe-35Mn could be considered compatible with the cells. It is then suggested that the Fe-35Mn alloys is a potential biocompatible and degradable biomaterial.
2.4.4 Summary

In summary, the ferromagnetism of Fe can be altered by adding Mn element. The resultant Fe-Mn can be non-ferromagnetism depending on the compositions. This becomes the most dominant factor of choosing Mn. Fe-35Mn alloys could be a good candidate for biodegradable applications because they demonstrate good mechanical properties, a suitable corrosion rate, non-magnetization, non-cytotoxicity and hemocompatibility. The main benefits (effects) of alloying Fe with 35wt.% Mn are summarized below:

(i) With the addition of 35wt.%Mn, there is no significant effect on grain size.
(ii) $\gamma$-Fe is the main phase in Fe-35Mn binary alloy which contributes to the MRI compatibility.
(iii) Fe-35Mn binary alloys show satisfactory tensile properties (YS, UTS, elongation and hardness) [81].
Fe-35Mn alloys show a higher corrosion rate than pure iron, but lower than Mg alloys [13].

Fe-35Mn alloys show good cell viability and low concentration of Mn ion release in the extraction media, providing confidence in the potentiality of biomedical applications [13].

There is no doubt that Fe-35Mn has drawn increasing attention in biomaterials field. However, the fully dense Fe-35Mn alloys invented by Hermawan et al. [3, 13, 94] still has some limitation on the degradation rate. It also should be noted that this alloy is still in its very early developmental stage. There is very limited number of reports available in the literature and obviously more research on the improvement of the degradation rate and cell or blood compatibility is urgently needed.

2.5 Production of Fe-35wt.%Mn alloys by powder metallurgy

It is well known that casting and forging are two of the commonest metalworking processes. It is therefore no surprise that the Fe-Mn alloys are usually fabricated by these techniques. Powder metallurgy (PM) is an alternative production approach which has evolved over the past a few decades. PM is the process of blending fine powdered materials, pressing them into a desired shape or form (compacting), and then heating the compressed material in a controlled atmosphere to bond the material (sintering). The PM process generally consists of four basic steps: (1) Powder production and preparation. Powders can be pure metal powders or their alloys, nonmetals and other compounds; (2) Powder blending or mixing. In this step, alloying element or pressing lubricant can be involved; (3) Powder shaping. A die and punches would be normally used in this step; (4) Sintering. During the sintering process, the powder particles are densified through atomic diffusion. The integrity and strength of the powdered compact is achieved by sintering. Optional secondary processing often follows to obtain special properties or enhanced precision [95]. A flow chart of PM process is shown in Fig. 2.11.
Some valuable features of PM compared with traditional casting and forging methods are:

(vi) Low product cost: lower energy consumption, higher material utilisation and reduced numbers of process steps;

(vii) Ability to produce products with complex geometrical shapes;

(viii) Ability to obtain some uncommon characteristics of the products by the starting feedstock, such as chemical constituents, microstructure and porosity;

(ix) Ability to fabricate a wide range of products compared with direct alloying of materials, and to manufacture components which would otherwise disintegrate or decompose;
Processing of materials with very high melting points. Such metals are very difficult to produce by melting and casting and are often very brittle in the cast state. Tungsten, molybdenum and tantalum are such examples.

Controlled levels of porosity could be obtained.

PM technologies have been applied to the development of the biodegradable Fe-Mn alloys. A conventional blend-press-sinter method, followed by cold rolling was reported by Hermawan et al in 2008 [3]. The processing via PM was successful in terms of achieving the necessary mechanical properties. However it is noted that the degradation rate of the developed Fe-35Mn alloy was still too low. Therefore, one of our objectives in this research is to explore new procedures to fabricate less dense Fe-35Mn with controlled porosity. The introduction of the porosity is beneficial, not only for degradation rate, but also for tissue ingrowth. The main processing techniques involved in this study are introduced in the following sections.

2.5.1 Powder mixing

Powder mixing is a process by which two or more different component powders are uniformly mixed. Mixing quality would not only affect the shaping process and the quality of the compacts, but also seriously affect the sintering process and the quality of final products. There are two methods of mixing: mechanical mixing and chemical mixing; the mechanical mixing is the most common technique and there is introduced here.

Commonly used machines for mechanical mixing are ball mill mixer, V-blender, conical mixer and spiral mixer, etc. Mechanical mixing includes dry mixing and wet mixing. Dry mixing is commonly used in producing iron-based products. Carbide alloy mixtures are normally prepared by wet mixing method. The commonly used liquid media for wet mixing are ethanol, gasoline and acetone, etc. In order to ensure that the wet mixing process can be carried out successfully, wet mixing media (1) do not chemically react with the material, (2) should not have a low boiling point or be volatile, (3) should be non-toxic, (4) should be resourceful and with low cost.

In some cases, the powder particle size is too big and hence causes compaction and sintering problems. Large particles need a higher compaction pressure and usually result in a low green density, which further leads to a low sintered density in the final product.
Therefore, reduction in particle size is required. One technique for reducing particle size is mechanical milling (MMing). In addition to the particle size reduction, MMing can also lead to the formation of a fine microstructure. In the two-component powders, it is often to form a fine-grained composite microstructure. Such fine composite microstructure promotes the densification process during sintering, as the diffusion pathway between the particles is reduced.

2.5.1.1 Mechanical milling (MMing) and alloying (MAing)

MMing or MAing is a powder preparation technique which has been developed in the last two decades. In MMing or MAing process, a suitable powder charge (typically, a blend of elemental powders) with a suitable milling medium is placed in a high energy mill. Vigorous shock and collision from milling media (balls) to powder particles, repeating deformation, breakage and welding together between the powders happen. In some cases, mutual diffusion and solid-state reaction happen. A schematic diagram of MMing is shown in Fig. 2.12. MAing is only named, if alloy or compound powder forms when the milling time is sufficiently long.

The objectives of MMing are to reduce the particle size and change particle shape, to mix and blend and to synthetize nanocomposite. The typical high energy mill instruments include tumbler ball mills, vibratory mills, planetary mills, and attritor mills. [96]. The kinetics of MMing depends on the energy transferred to the powder from the balls during milling [97]. Many parameters would affect the energy transfer, including mill types, milling speed, ball size and size distribution, dry or wet milling, milling temperature and milling time.
2.5.1.2 Space-holding method for producing porous materials

New processes have recently been developed to synthesize biomimetic porous scaffolds through PM. It is an efficient technique for manufacturing complex shapes with interconnected pores without the need for machining steps. In particular, the space holder sintering method is capable of adjusting the pore shape, the porosity, and the pore size distribution.

A solid space holder normally consists of solid powders which can be easily removed, either by a post sintering process at low temperatures or by dissolving in a solvent, without causing excess contamination of the product. This is also a common way to make an open cell foam [98]. The metal powders are mixed with the solid space holder and then pressed in to a compact. This allows sufficient green strength to be imparted to the metal powder to prevent collapse when the space holders are removed. Sintering is the final step. The typical space holder process is indicated in Fig. 2.13.
Some explored spacer materials include sodium chloride [100-102], potassium chloride, potassium sorbate, or a mixture thereof [103], sodium bicarbonate [104], PMMA [101, 105], carbamide (urea) powders [99, 106, 107], ammonium hydrogen carbonate particles [99, 108], polymer granules [109], magnesium powder [106, 110]. Fig. 2.14 and Fig. 2.15 show some typical porous microstructure images of samples produced by space holder technique.

Figure 2.14 - Scanning electron micrograph of the porous structure of TiNi alloy foam with 71% porosity with NH$_4$HCO$_3$ as space holder material.[111]
Currently, there is limited literature on porous iron or iron-based alloy as a scaffolding material. Porous Fe has been fabricated via either CO-CO$_2$ gas foaming process [113] or the use of polymer foaming agent [109, 114]. In 2000, Jee et al. produced metal foams with a porosity >90% by a novel PM route using polymer as space holding materials. In 2007, a method for manufacturing iron foam using CO and CO$_2$ as foaming gases was studied by Murakami et al. In 2010, the open porous Fe and Fe-phosphorous alloys had been produced by Quadbeck et al. via a replication route as biodegradable bone replacement [114]. However, those techniques are in general complex, as compared with space holding technique in which only metal powder and space holding particles are involved.

In summary, space holding method is viewed as the most promising methods to fabricate biodegradable metallic forms that have optimized pore morphology, by simply selecting and sieving the right type and size of the space holder.

Figure 2.15 - NiTi alloys with the addition of space-holder (urea) materials (porosity versus $r_s$=0.20, 0.40 and 0.70 from left to right) (a) optical microscopy and (b) scanning electron microscopy [112].
2.5.2 Powder compaction

Powder compaction is the process of compacting metal powder in a die through the application of high pressures. During the external force compaction, large gaps are filled up, oxidation films on the particle surface are crushed and contacting areas between particles increase with the movement and deformation of the powder particles [115]. A schematic illustration of this process is shown in Fig. 2.16. In this study, two compaction methods were used: die pressing and cold isostatic pressing (CIPing).

![Schematic illustration of powder compaction process.](image)

**Figure 2.16 - A schematic illustration of powder compaction process.**

**Die pressing**

As the name suggests, the powder is pressed in a die. Die pressing is the most dominant technology for forming PM products. This forming technology involves a production cycle comprising of: loading powder to the die, compaction of the powder within the die with the plungers (punches) to form compact, and removal of the compact.
Because the die wall friction, the green density in a compact is usually inhomogeneous. Isostatic pressing can largely rectify the uneven green density distribution in the compact.

**Cold isostatic pressing (CIPing)**

The force by isostatic pressing is directly exerted onto powder pallets or indirectly on some elastic covers. A uniform force is applied to the powders from every direction at the same time. In this way powder compacts could achieve uniform density distribution and higher strength. Isostatic pressing can be performed at room temperature (cold isostatic pressing – CIPing) or high temperatures (hot isostatic pressing – HIPing). In fact, HIPing is a common post metal-forming technique to close the micropores in the casting. CIPing usually follows die pressing. Consequently, CIPed compacts have higher density, much more uniform and better mechanical properties compared with die pressing compacts.

### 2.5.3 Sintering

The final processing step is sintering. Sintering is a micro-welding process for bonding powder particles together into a solid structure via mass transport that occurs largely at the atomic level [116]. In the current work, a solid state sintering was adopted. In the solid state sintering process, no liquid phase evolves. The densification is obtained by solid state diffusion [117].

A sintering process has four main stages, namely an adhesion stage (formation of powder contact), an initial stage (neck growth proceeds rapidly but powder particles remain discrete), an intermediate stage (isolated pores tend to become spheroidal and densification occurs) and a final stage (pores close and densification comes to the final stage). Each sintering stage displays different geometric forms, as illustrated in Fig. 2.17. The pore structure is irregular at the initial stage, depending on the green powder packing structure. As the pore structure becomes rounded, discrete particles are less evident and the solid structure is more coherent. The sintering process is sensitive to many factors, such as particle size and shape, sintering parameters and green density. Table 2.10 highlights some key processing changes during sintering.
Figure 2.17 - A schematic diagram of the four sintering stages starting with a loose powder structure [116].
Table 2.10 - Effect factors in the sintering process [116].

<table>
<thead>
<tr>
<th>Change of processing parameters</th>
<th>Positive or neutral effects</th>
<th>Negative effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decrease in particle size</td>
<td>Faster sintering</td>
<td>Greater expense</td>
</tr>
<tr>
<td>Increase in sintering time</td>
<td>Grain growth and coarsening</td>
<td>Reduction of productivity Greater expense</td>
</tr>
<tr>
<td>Increase in sintering temperature</td>
<td>Grain growth</td>
<td>Greater expense</td>
</tr>
<tr>
<td></td>
<td>Higher properties</td>
<td>Less precision</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Greater shrinkage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Furnace limitation</td>
</tr>
<tr>
<td>Increase in green density</td>
<td>Less shrinkage</td>
<td>Density gradients</td>
</tr>
<tr>
<td></td>
<td>Smaller pores</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Higher final density</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Uniform dimensions</td>
<td></td>
</tr>
<tr>
<td>Increase in alloying/additives</td>
<td>Higher strength</td>
<td>Homogeneity problems</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Higher sintering temperatures Furnace limitations</td>
</tr>
<tr>
<td>Use of sintering aids</td>
<td>Faster sintering</td>
<td>Enbrittlement</td>
</tr>
<tr>
<td></td>
<td>Lower sintering temperatures</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Grain growth control</td>
<td>Distortion</td>
</tr>
</tbody>
</table>
2.6 Potential biomedical applications of Fe-35wt.%Mn alloys

As Fe-35Mn is a metallic biodegradable material, it has the nature of having higher strength than polymers for supporting loads, and greater plasticity than bioceramics. Thus, two applications are considered potential for Fe-35Mn alloys, including cardiovascular implants (i.e. stents) and orthopaedics (i.e. bone replacement and regeneration). These are further introduced in the following sections.

2.6.1 Coronary artery stenting

Coronary heart disease is normally caused by the abnormal lipid metabolism in the human body. The lipid which cannot be metabolized in blood would deposit on the inner vascular wall (used to be smooth). As the deposition accumulates, some white porridge-like plaques would be formed on the endarterium. This whole process is called artery atherosclerosis. With the plaques gradually increasing, the arterial lumen gradually gets narrower. This causes a blockage of blood flow, leading to cardiac ischemia and finally angina. At current stage, there are three main treatments for coronary heart disease: medication treatment, surgery treatment (bypass) and interventional treatment. Intervention treatment is the most widely used and the effect is the most effective. Coronary stent is the key device of interventional therapy. A schematic diagram of interventional stent treatment is illustrated in Fig. 2.18. A stiff wire was inserted to support the aortic arch passage and the device was finally positioned within the diseased aortic valve. The extracorporeal circulation, advanced, was then started and by pulling back the delivery sheath the stent was deployed successfully. The final supraaortic angiogram revealed a well-positioned prosthesis without evidence for aortic regurgitation. A laser engraving machine is used to cut seamless thin-walled metal tube to a mesh pattern. The metal mesh is then treated by pickling, polishing and drug loading subsequently to complete the final stent.
Figure 2.18 - Implantation of the self-expanding stent at different stages, from Grube et al. [118].
At present, the corrosion resistant (or permanent) stents are widely used. Stents made of biodegradable material are under research and development. This is a new technological approach in accordance with the new understanding of clinical events in the arterial wall during and after stent implantation. The biodegradable stent offers a temporary opening to a narrowed arterial vessel until the vessel remolds. It will then be corroded and absorbed gradually after its scaffolding period. This might be providential, for example, in treating congenital heart disease in growing babies [14].

An ideal biodegradable stent should be able to compromise its degradation and mechanical integrity during implantation, as illustrated in Fig. 2.19. Ideally, degradation should begin at a very slow rate in order to maintain the optimum mechanical integrity of the stent during the arterial vessel remodelling process. A period of 6–12 months is expected for the remodelling process to be completed [14, 119, 120]. Thereafter, when the mechanical integrity decreases, the degradation accelerates at a higher rate without causing an intolerable accumulation of degradation product around the implantation area and systemic organs [121]. A total period of 12–24 months after implantation is expected and considered reasonable for the stent to be totally degraded [121, 122]. The mechanical integrity and degradation behavior are influenced by the type of stent material itself. Nowadays the research on enhancing the degradation behavior of stenting material while maintaining its mechanical integrity becomes the hotspot in heart-stenting area.

![Figure 2.19 - Illustration of an ideal compromise between mechanical integrity and degradation of a biodegradable stent, from Ref. [14].](image-url)
2.6.2 Orthopaedics

Theoretically, almost all the materials used in orthopaedics surgeries are biomaterials. Throughout the history of the development of orthopaedics surgery, biomaterials have played a vital role in the success of the orthopaedics surgery. Some common absorbable orthopaedic materials are collagen, sodium hyaluronate, chitosan and some novel metallic degradable materials. Their typical clinical applications are listed in Table 2.11. In recent years, a number of biodegradable materials have been under rapid development.

Table 2.11 - Clinical applications of some typical orthopaedic materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collagen</td>
<td>Filling materials, Stents, Artificial vessels and skin</td>
</tr>
<tr>
<td>Sodium hyaluronate</td>
<td>Filling materials, Cartilage nonwovens, Microporous</td>
</tr>
<tr>
<td>Chitosan</td>
<td>membrane</td>
</tr>
<tr>
<td>Bioabsorbable metals (Mg, Fe, etc.)</td>
<td>Filling gel, Anti-adhesion hemostatic agent, Tissue</td>
</tr>
<tr>
<td></td>
<td>engineering scaffolds</td>
</tr>
<tr>
<td></td>
<td>Tissue engineering scaffolds (porous bone)</td>
</tr>
</tbody>
</table>
Chapter 3 Experimental

This chapter describes the experimental procedures used throughout the present research, which include sample preparation, microstructure characterization, mechanical testing, corrosion behavior investigations and cell compatibility assessment. The detailed procedures are described below.

3.1 Sample preparation

3.1.1 Powder preparation

The starting metal powders were elemental iron (Fe) and manganese (Mn) powders, with specification as presented in Table 3.1. The SEM images of these two powders are shown in Fig. 3.1. Both powders were of irregular shape, typical characteristic of electrolytic powders. Ammonia bicarbonate (NH$_4$HCO$_3$) powder was used as a pore-forming agent (porogen).

Fe and Mn powders, with a nominal composition of 65wt.%Fe-35wt.%Mn, were gently blended in a rotary blender for 4 and 10 hours with a ball-to-powder (B-P) weight ratio of 1:1. The 10-hour blended powder was used in chapters 4 and 6. The 4-hour blended powder was used in Chapter 5 for further mechanical milling (MMing).

MMing was conducted in a planetary ball mill (PM 100) for 6 hours with a B-P ratio of 5:1. An amount of 0.5 wt.% stearic acid was added as processing control agent (PCA) during ball milling.

In chapter 6, the 10-hour blended powder was then mixed with 10 vol.% and 20 vol.% NH$_4$HCO$_3$ in a planetary ball mill for additional 1 hour. Ethanol (2 vol.%) was added in the ball mill vial with the pre-mixed Fe-Mn powder and NH$_4$HCO$_3$ particles. The addition of ethanol was to promote uniform distribution of NH$_4$HCO$_3$ in the Fe-Mn powder mixture.
Table 3.1 - Characteristics of starting materials used in this thesis

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Suppliers</th>
<th>Mean size (µm)</th>
<th>O (%)</th>
<th>S (%)</th>
<th>C (%)</th>
<th>Si (%)</th>
<th>P (%)</th>
<th>Bal. (%)</th>
<th>Powder morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Sigma-Aldrich</td>
<td>40</td>
<td>0.15</td>
<td>0.05</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>97.6</td>
<td>irregular</td>
</tr>
<tr>
<td>Manganese</td>
<td>Sigma-Aldrich</td>
<td>35</td>
<td>0.01</td>
<td>0.07</td>
<td>0.02</td>
<td>0.05</td>
<td>0.01</td>
<td>98.4</td>
<td>irregular</td>
</tr>
</tbody>
</table>

**3.1.2 Die compaction**

The powder mixtures after thorough mixing or after MMing were pressed with a uniaxial hydraulic press at a pressure ranging from 200 MPa to 600 MPa. In some cases, cold isostatic pressing (CIPing) at 200 MPa was used after die compaction (Chapter 5).
3.1.3 Debinding

In the case of the use of porogen NH₄HCO₃ (Chapter 6), the debinding of NH₄HCO₃-containing Fe-35Mn green compacts was carried out in a horizontal tube furnace with a controlled argon flow rate of 150ml/min. The heating profile is shown in Fig. 3.2.

![Figure 3.2 - Thermal debinding process for porogen removal.](attachment:debinding_graph.png)

3.1.4 Sintering

Essentially all the compacted samples, regardless of how they were processed, need to be sintered at high temperatures to attain necessary mechanical properties. The sintering parameters in chapters 4, 5 and 6 are presented in Table 3.2. The compacted pellets in Chapter 5 were sintered in a horizontal tube furnace at 950° in a nitrogen flow atmosphere for 8 hours. The sintering for the green compacts in chapters 4 and 6 was undertaken in a high vacuum furnace (3×10⁻³ Pa). The effects of sintering parameters on the resulting microstructures, physical properties and mechanical properties were investigated. The sintering scheme is shown in Table 3.2.
Table 3.2 - Sintering parameters used in chapters 4, 5 and 6.

<table>
<thead>
<tr>
<th>Sintering Parameter</th>
<th>Chap 4</th>
<th>Chap 5</th>
<th>Chap 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>1000/1100/1200</td>
<td>950</td>
<td>1200</td>
</tr>
<tr>
<td>Heating rate, °C/min</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Holding time, hour</td>
<td>2/4</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>vacuum</td>
<td>nitrogen</td>
<td>vacuum</td>
</tr>
</tbody>
</table>

3.2 Measurement of density, porosity and open porosity

Before measuring, all the sintered compacts were first mechanically ground up to 2000 grit and then ultrasonically cleaned. At last, the ground compacts were vacuum dried overnight.

Density of all the sintered samples was calculated by the Archimedes’ principle, as specified in the ASTM standard B962-13. The open porosity was measured as per the ISO 2738 standard. The samples were vacuum dried overnight until a constant weight was obtained. Then, the dried compacts were vacuum impregnated overnight with distilled water to measure the saturated weight. The saturated sample was placed on a support in water and the suspended weight was noted. The theoretical density of Fe-35Mn is 7.63 g/cm³. The density of water (ρ_water) depends on the temperature. The following equations were used to calculate the total porosity and the open porosity of the sintered Fe-35Mn compacts.

\[
\text{Fractional Density} = \frac{\text{Dry weight}}{(\text{Saturated weight} - \text{suspended weight}) \times 7.63} \times \rho_{\text{water}} \times 100\% \\
\text{(Eq. 3.1)}
\]

\[
\text{Total Porosity} = 100\% - \text{Fractional Density} \\
\text{(Eq. 3.2)}
\]

\[
\text{Open Porosity} = \frac{\text{Saturated weight} - \text{Dry weight}}{\text{Saturated weight} - \text{suspended weight}} \times \rho_{\text{water}} \times 100\% \\
\text{(Eq. 3.3)}
\]
\[ \rho_{\text{water}} = 1.0017 - 0.2315 \times \text{Temperature at measurement} \quad \text{(Eq. 3.4)} \]

The pore analyses were carried out using a BET instrument (Autosorb-1, Quantachrome).

### 3.3 Characterization of microstructures

Phase constituents of the sintered samples were identified using X-ray Diffraction (XRD) analysis (Philips PW 1710) with a monochromatic Cu-K\(\alpha\) source, operated at 40 kV, 40 mA and at a scanning rate of 0.02°/s between 2\(\theta\) of 30° to 80°.

Optical microscopy (Olympus BX60) was used to observe the microstructures of the sintered Fe-35Mn alloys. Metallographic samples were mechanically ground using various grits of SiC papers (220, 600, 1000 and 2000) sequentially, followed by final polishing with 6µm and then 3µm diamond paste. The polished sections were subsequently etched for approximately 35s using 2% Nital reagent.

An environmental scanning electron microscope (ESEM, Philips XL 30s-FEG) was used to examine the mechanically polished sections of the sintered Fe-35Mn surface, corroded surfaced and the fracture surfaces of the tensile specimens. All samples were coated with a thin film of Au using an ion sputter (E1030, Hitachi). Backscattered electron imaging was performed on the above system, equipped with a Robinson Detector module.

Energy dispersive x-ray analysis of the samples was performed on the above system equipped with a Kevex Quantum Window x-ray detector, passed through a signal processor (Model 500, IXRF Sustems Inc.) and analysed using the EDS Thermo Noran System SIX.

### 3.4 Corrosion evaluation

#### 3.4.1 Sample preparation

For both electrochemical and immersion corrosion tests, samples were first mechanically ground up to 2000 grit, polished with 6 µm diamond paste, rinsed with deionized water, and finally ultrasonically cleaned. Sample sizes for electrochemical corrosion tests were round pellets with the dimension of \(\phi=16\text{mm}\) and \(h=4\text{~}5\text{mm}\). These round samples were further cut by an electric discharge CNC wire cut machine to a cubic \(10\times10\text{mm}\).
3.4.2 Corrosion media

The electrochemical and immersion corrosion studies were carried out in two media: 5wt.% NaCl and simulated body fluid (SBF). The ion concentrations of the SBF medium is listed in Table 3.3 [123].

Table 3.3 - Nominal ion concentrations of SBF solution in comparison to those in human blood plasma [123].

<table>
<thead>
<tr>
<th>Ion</th>
<th>Blood plasma</th>
<th>SBF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+</td>
<td>142.0</td>
<td>142.0</td>
</tr>
<tr>
<td>K+</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Mg2+</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Ca2+</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Cl-</td>
<td>103.0</td>
<td>147.8</td>
</tr>
<tr>
<td>HCO3-</td>
<td>27.0</td>
<td>4.2</td>
</tr>
<tr>
<td>HPO4-</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>SO42-</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.2~7.4</td>
<td>7.40</td>
</tr>
</tbody>
</table>

3.4.3 Electrochemical analysis

Electrochemical studies of the Fe-35Mn alloys were carried out using an electrochemical workstation (CHI650C) in two corrosion media described above: 5% NaCl and SBF solutions by potentiodynamic polarization techniques and electrochemical impedance spectroscopy (EIS) measurements.
A standard three-electrode system was adapted including the polished Fe-35Mn alloy sample with 1 cm$^2$ exposed area as the working electrode, a Pt plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrochemical properties of the Fe-35Mn alloys were initially evaluated based on an open circuit potential (OCP). Electrochemical impedance measurements were recorded at OCP, +0.2V and +0.5V OCP after a 1800 seconds exposure time and in the frequency range from 105Hz to 0.01mHz using AC amplitude of 10 mV. In order to ensure the reproducibility of the results, the experiments were performed in at least triplicate.

The polarization studies were carried out in the potential range -1.5V to 0 (at least around ±250mV from OCP vs SCE). The polarization curves were recorded at a constant sweep speed of 0.2mV/s. The corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) were determined from the polarization curves using Tafel method. The degradation rate was evaluated by the following equation according to the ASTM G59 standard:

$$CR_{pd} = 3.27 \times 10^{-3} \frac{i_{corr} \cdot EW}{\rho}.$$  

(Eq. 3.5)

Where $i_{corr}$ is in mA/cm$^2$, $\rho$ is the density and EW the equivalent weight. A density of 7.63 g/cm$^3$ and an equivalent weight of 27.92 g were used for the Fe-35Mn alloy. The value of $i_{corr}$ was derived from the polarization curves with the polarization resistance (Rp) method.

### 3.4.4 In vitro immersion test

Samples for the immersion tests were mounted with 1cm$^2$ exposure area. For the static immersion test, specimens were immersed in a 60ml solution (5% NaCl or SBF) at room temperature. After 1, 3, 5, 7 and 14 days, specimens were taken out, rinsed with distilled water and ethanol, and finally vacuum dried overnight for the weight loss measurement.

Based on a pioneering work of Levesque et al.[92], a dynamic immersion test bench was designed to mimic the blood flow inside the coronary artery, shown schematically in Fig.3.3. In this circulation system, the flow velocity was set at 10 cm/s; it is noted that blood flow velocities in human vessels range from 0.03 to 40 cm/s (aorta: 40 cm/s, capillaries: 0.03 cm/s, vena cavae inferior and superior: 15 cm/s) [124, 125]. Mounted specimens were placed in the testing solutions at the bottom of the container. All
specimens were exposed to the dynamic fluid flow (SBF solution) for 1, 3, 7, 14 and 30 days. When the test was over the specimens were removed, rinsed with distilled water and ethanol, and vacuum dried.

The concentrations of released iron and manganese ions during dynamic immersion tests were measured by flame atomic absorption spectrometry (FAAS, Varian SpectrAA 50). The instrument parameters for the ion concentration measurements by FAAS are summarized in Table 3.4.

For each Fe-35Mn sample, the Fe and Mn ion concentration released into SBF during every 2 days was recorded and accumulated to find out the Fe and Mn ion released over 7 and 30 days in a simulated physiological environment.

Before the FAAS test, all the solution samples were first acidified by adding one drop of concentrated nitric acid into each tube, and then filtered to eliminate any precipitates. The filtered solutions were tested by FAAS and three readings were recorded for each solution sample.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Lamp current (mA)</th>
<th>Flame stoichiometry</th>
<th>Bandwidth (nm)</th>
<th>Fuel</th>
<th>Support</th>
</tr>
</thead>
<tbody>
<tr>
<td>232.0</td>
<td>4</td>
<td>oxidizing</td>
<td>0.2</td>
<td>acetylene</td>
<td>air</td>
</tr>
</tbody>
</table>

The immersion corrosion products on the sample surface were removed by gently brushing the sample in a 15 % H₂SO₄ solution [54], ethanol cleaned and vacuum dried before being weighed. The corrosion rate (CR) was calculated based on the weight loss of specimens according to the ASTM G31-12a standard.

\[
CR_{im} = 8.76 \times 10^4 \frac{W}{A \cdot t \cdot \rho}
\]  

(Eq. 3.6)
Where the degradation rate is in mm/year, $W$ is the weight loss (g), $A$ is the exposure area (cm$^2$), $t$ is time of exposure (hour), and $\rho$ is the theoretical density of the sample (g/cm$^3$).

The morphology of the corroded surface after immersion tests was examined with an environmental scanning electron microscope (ESEM, Philips XL 30s-FEG) and the chemical compositions of the degradation products were analyzed using an energy dispersive spectrometer (EDS).

![Figure 3.3 - Schematic diagram of circulating corrosion system.](image)

3.5 Mechanical properties

3.5.1 Hardness testing

The Rockwell hardness was measured using a Wilson Rockwell hardness tester. Scale H was used in this test. At least 5 readings were recorded and the average value was used as the reported hardness. The standard deviation was calculated. Vickers microhardness was measured with a microhardness tester. The load used was 50 gf and dwell time was 30 seconds. At least 7 readings were made and the average value was used as the reported hardness.
3.5.2 Tensile testing

Tensile testing of the Fe-35Mn sintered compacts were carried out at room temperature using an Instron3367 tensile testing machine at a crosshead speed of 0.2 mm/min (corresponding to an initial strain rate of $4.12 \times 10^{-4}$ s$^{-1}$). Dog-bone shaped specimens for tensile testing (shown in Fig. 3.4), with a rectangular gauge cross section of $2 \times 2$ mm$^2$ and a gauge length of 8 mm, were wire electric discharge machined from the sintered compacts. The tensile specimens were ground and polished using 600, 1000 and 2000 grit SiC papers. A strain extensometer was clipped on to the test pieces to measure the elongation.

![Figure 3.4 - The sketch of tensile testing sample (scale 4:1).](image)

3.5.3 Slow strain rate tensile testing (SSRT)

The stress corrosion cracking (SCC) assessment was performed by a slow strain rate tensile (SSRT) testing method [126]. The geometry and dimensions of the SSRT testing
samples were the same as the tensile samples as shown in Fig. 3.4. The test pieces were cut from the sintered compacts made from both BE and MMed powders. The gauge section was ground progressively with SiC papers up to 2000 grit, followed by rinsing with ethanol before the SSRT. The exposed area of the test specimen was restricted to the gauge length by using Teflon tapes to wrap the rest of the specimen, thus, maintaining the constant area for exposure to the corrosive solution. The schematic of the experimental set-up of the SSRT rig is shown in Fig. 3.5. The tensile specimens were pulled at two different strain rates of \( \times 10^{-5} \text{ s}^{-1} \) and \( \times 10^{-6} \text{ s}^{-1} \) (corresponding to the crosshead speeds of 0.02 and 0.002 mm/min) until the fracture. The procedure complies with the ISO standard 7359–Part 7. All the tests were conducted at room temperature.

The testing solutions conducted in this assessment were 5% NaCl and SBF solution. 5ml of solution was replaced for every 3 hours during long period tests to ensure that the solution was always fresh and conducive for this experiment. For comparison, the SSRT tests were also performed in air under the same strain rates.

Figure 3.5 - The schematic of the experimental set-up of the SSRT system.
3.5.4 Assessment of stress corrosion cracking (SCC) susceptibility

The SCC susceptibility is indicated by the so-called SCC susceptibility index (I_{SCC}) obtained from a formula derived from the stress-strain curves by Abe et al.[127] and is given as:

\[ I_{SCC} = \frac{1 + \varepsilon_n}{1 + \varepsilon_{SCC}} \times \frac{P_n}{P_{SCC}} \]  

(Eq. 3.7)

Where \( \varepsilon_n \) and \( P_n \) are strain and load at maximum load obtained in the controlled environment (air); \( \varepsilon_{SCC} \) and \( P_{SCC} \) are strain and load at maximum load obtained in the corrosive environment. The larger the I_{SCC} value, the higher the specimen’s susceptibility to stress corrosion cracking. In this study, this susceptibility index is denoted by I_{SCC}.

3.5.5 Fractography

The fractured surfaces of the testing samples were immediately removed, ultrasonically cleaned by ethanol and vacuum dried after SSRT. The fractography of the fractured surface was carried out using an environmental scanning electron microscope (ESEM, Philips XL 30s-FEG) at 20kV.

3.6 Cell compatibility

3.6.1 Extraction preparation

Fe-35Mn alloy SBF extraction were prepared by an incubator shaker (Innova 44) The specimens with approximately 15mm\(^2\) surface area were firstly ground with SiC sand papers and cleaned according to instructions for preparing the immersion samples (see Section 3.4.1). After that, the specimens were sterilized in 70% ethanol for 5 min, washed three times in SBF, and finally immersed in 100 ml SBF at 37 °C for 24 h and agitated at 200 rpm in the shaker.

Before conducting cell experiments, FAAS was used to measure the released Fe\(^{2+}\) and Mn\(^{2+}\) ion concentrations of the extraction. Before the FAAS measurement, the stored SBF solutions were first acidified by adding one drop of concentrated nitric acid into each tube, and then filtered to eliminate any precipitates. The filtered SBF solutions were tested by FAAS and three readings were recorded.
3.6.2 Biocompatibility and cell viability

The cell compatibility test was performed by an indirect contact method. Murine fibroblast cell line L929 (ATCC CCL-1) was used to evaluate the compatibility of the Fe-35Mn alloy extraction. The cell-culture medium (following called medium in short) contains Dulbecco's modified Eagle's medium (DMEM) with 10% fetal calf serum (FCS) – both DMEM and FCS were supplied by Life Technologies. Cell proliferation was measured using a resazurin fluorescence assay, which is used to quantify viable cells at various stages of proliferation.

In order to investigate the cell viability in the Fe^{2+} and Mn^{2+} containing SBF media, different iron concentration levels were selected. By doing so, various volumes of extraction (2, 10, 20, 100 and 200μL) were added in to each cell well. The bare SBF medium, which did not contain any Fe^{2+} or Mn^{2+} ions, was used as the control. The total medium amount remained constant at 1mL per well. The extraction, SBF and medium for each well are listed below in Table 3.5.

Table 3.5 - Recipes for cell test wells.

<table>
<thead>
<tr>
<th>Specimen ID</th>
<th>SBF extraction µL</th>
<th>SBF µL</th>
<th>Medium µL</th>
<th>Cells (Y/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>198</td>
<td>800</td>
<td>Y</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>190</td>
<td>800</td>
<td>Y</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>180</td>
<td>800</td>
<td>Y</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>100</td>
<td>800</td>
<td>Y</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>0</td>
<td>800</td>
<td>Y</td>
</tr>
<tr>
<td>SBF control</td>
<td>0</td>
<td>200</td>
<td>800</td>
<td>Y</td>
</tr>
<tr>
<td>Medium control</td>
<td>0</td>
<td>0</td>
<td>1000</td>
<td>Y</td>
</tr>
<tr>
<td>Blank</td>
<td>0</td>
<td>0</td>
<td>1000</td>
<td>N</td>
</tr>
</tbody>
</table>
At the start of each experiment, the L929 mammalian cells were cultured in the aforementioned cell-culture medium (DMEM with 10% FCS) at 37 °C in a humidified atmosphere of 5% CO₂. The cultured cells were placed on a 24-well tissue culture plate (TCP). Then L929 cells were seeded at the well bottom with a concentration of 1x10⁴ cell/mL in 1mL cell-culture medium for each well (except for the blank). Trypan blue exclusion was used to enumerate live cells.

The cells were incubated at 37°C in air (5% CO₂) for 24 h, after which the cell-culture medium was replaced with 1 mL of 500μl resazurin solution and incubated for 4 h. The supernatant was collected and centrifuged at 2000 rpm for 5 min at room temperature to pellet any cells. 100μl of the centrifuged supernatant was aliquoted in triplicate into a 96-well black microtitre plate and the fluorescence value was recorded at 530 nm excitation and 590 nm emission using a Perkin Elmer Enspire 2300 Multilabel Reader.

After the 1st day’s fluorescence reading, the Fe-Mn SBF extractions in SBF (extraction/SBF) at various volumes ranging from 2/200 to 200/200μl and SBF control with 800μl cell-culture medium were added to the wells. The cells were incubated for another 3 days. Cell proliferation measurement was repeated daily. Fresh extractions, SBF and cell-culture medium were added after the reading. Before obtaining the fluorescence reading on the first and fourth day, the wells with cells were imaged using an optical microscope.
Chapter 4 Powder Sintering from Blended Elemental (BE) Powder Mixture

4.1 Introduction

Powder metallurgy (PM) has been taken into account for lowering the cost of iron alloy machine parts. PM iron-based alloys can be classified into three categories: pre-alloyed PM alloys, rapid solidified PM alloys and blended elemental (BE) PM alloys according to the adoption of raw powder. Use of BE powder is more cost-effective, due to cheap iron and other elemental powders. Commonly used iron powder includes atomized iron powder, reduced iron powder and electrolyte iron powder.

Sintering, in PM, is one of the most important technological process, which is defined as a micro-welding process for bonding powder particles together into a solid structure via mass transport that occurs largely at the atomic level [116]. The influences of sintering conditions on the densification of compacts in PM have been well studied [116, 128]. A large number of researchers have investigated the sintering effects of sintered compacts prepared by different PM routes, such as the effects on final density level, pore characteristics and mechanical properties [129-132]. The thermodynamics of densification [133, 134] and diffusion mechanisms [135-138] during sintering process have been studied by establishing some theoretical models.

In this chapter, the recent progress in the production of PM iron-manganese alloys by a simple blend-press-sinter method was reported. Various sintering temperatures and holding times were conducted in this chapter. The effect of sintering parameters on the porosity, microstructure, the mechanical properties and corrosion resistance of the Fe-35wt.%Mn alloys were also systematically investigated.
4.2 Processing

These raw powders were blended, according to the required composition: 35wt.%Mn and 65wt.%Fe in a high-efficiency blender for 10 h, followed by uni-axial pressing under a pressure of 400 MPa. The powder compacts were sintered at a temperature ranging from 1000 to 1200 °C for 4 h in a vacuum sintering furnace with a vacuum level of $5 \times 10^{-3}$ Pa, followed by furnace cooling. The heating profile applied in this chapter is listed below in Fig. 4.1.

![Figure 4.1 - Heating profile of Fe-35Mn powder mixture sintered for 2 and 4 hours at three different sintering temperatures: 1000, 1100 and 1200 °C.](image-url)
4.3 Results and discussion

4.3.1 Density and porosity

Fig. 4.2 shows the porosities of the sintered Fe-35Mn compacts produced by BE powder mixtures under various sintering parameters. The porosities of the sintered compacts reduced with increasing sintering temperature and holding time. For instance, the compacts sintered at 1200 °C for 4 hours presented a porosity of 19.4%, which was lower than that sintered for 2 hours (27.0%) at the same temperature. It was also lower than that sintered at 1000 °C for 4 hours (32.0%). In other words, the higher sintering temperature and the longer sintering time, the higher sintered density (lower the porosity).

Figure 4.2 - Illustration of relationship between sintering parameters and porosity.
4.3.2 Phase constituents and microstructure

Figs. 4.3 and 4.4 show the ESEM microstructure of the sintered Fe-35Mn compacts at various sintering temperatures and holding times. As seen in Figs. 4.3 (a) and (b), the sintering was incomplete at 1000°C neither for 2 hours nor for 4 hours. There were a large number of interconnected and irregular pores (black color) with size ranging from 50μm to 100μm as shown in Figs. 4.3 (c) and (d). For all the sintering time, when sintering temperature increases to 1100 °C, the pore size was much smaller when compared with that sintered at 1000 °C, although some of the pores were still angular and elongated. When sintering temperature further rose up to 1200 °C, it was clear that both the pore size and porosity sharply decreased by a large extent. In addition, some spherical shaped pores transformed to crevices. These phenomena could be observed by comparing amongst Fig.4.3 (a), Fig. 4.4 (a) and Fig. 4.4 (c) or Fig. 4.3 (b), Fig. 4.4 (b) and Fig. 4.4 (d) as they were with the same holding time 2 and 4 hours respectively. The porosity values shown in Fig. 4.2 had corresponded to this as well.

Sintering temperature plays a dominant role for sample densification and pore elimination. It is recognized that sintering is a diffusion controlled process and the change of sintering temperature can significantly affect the atomic motion of Fe and Mn [137, 138].

The dependence of atomic motion of Fe and Mn atoms on temperature can be described using Arrhenius equation [139].

\[ D = D_0 \exp\left(\frac{-Q}{RT}\right) \]  

(Eq. 4.1)

where \( D \) is the diffusion coefficient, \( D_0 \) is the diffusion constant, \( Q \) is the diffusion activation energy, \( R \) is the ideal gas constant, and \( T \) is the absolute temperature.

Diffusion coefficients of Fe and Mn in the \( \gamma \)-austenite phase can be calculated according to Arrhenius equation. With the sintering temperature rising, the diffusion coefficient increased. Consequently, the increase of sintering temperature promotes the densification of the sample.

The sintering time is also a key influence factor on the microstructure and porosity of the sintered compacts. As indicated in Figs. 4.4 (a), (b) and Figs. 4.4 (c), (d), the longer
holding time led to a much denser morphology. By extending the sintering time, the density increased and the porosity decreased.

Figure 4.3 - ESEM images of Fe-35Mn compacts sintered at 1000°C for various holding time: (a) 2 hours; (b) 4 hours, (c) and (d), close up images of (a) and (b) respectively.
Chapter 4 Powder Sintering from Blended Elemental (BE) Powder Mixture

Figure 4.4 - ESEM images of sintered sample sintered at 1100 and 1200 °C for 2 and 4 hours: (a) T = 1100 °C, t = 2 hours; (b) T = 1100 °C, t = 4 hours; (c), T = 1200 °C, t = 2 hours; (d), T = 1200 °C, t = 4 hours.

Fig. 4.5 indicates the phase constituents of the sintered Fe-35Mn at different sintering temperatures between 1000 and 1200 °C for 2 and 4 hours. As illustrated, γ-austenite was the overwhelming phase in the compacts sintered at all temperatures. Interestingly, apart from the main γ-austenite phase (f.c.c.), a weak peak corresponding to ε-martensite phase (c.p.h.) was present as well.

The presence of martenstic ε phase seemed unexpected. However, Schumann detected ε phase using XRD, dilatometry and metallography [140]; he concluded that at room temperature the amount of ε phase largely depended on the Mn content in the Fe-Mn system. Later works further confirmed this finding [141, 142] and a diagram is presented.
in Fig. 4.6, showing the relationship between the fraction of each phase and the Mn content. It can be seen that the amount of $\varepsilon$ phase can be up to 50% if the quenched Fe-Mn alloy contains 15% to 23% Mn [89, 141]. In the alloys with Mn contents > 27 wt.% the $\varepsilon$ phase is not detectable [143]. Therefore the presence of martensitic $\varepsilon$ phase in our Fe-35Mn samples suggested some local compositional inhomogeneity. In other words, some regions should have a composition much less than 27 wt. % Mn. This was indeed confirmed by the EDS analysis. This much lower Mn concentration would promote the formation of $\varepsilon$ phase. It also implied that the $\gamma \rightarrow \varepsilon$ martensitic transformation occurred even under furnace cooling conditions, whose mechanism was unclear. It was noted that both austenitic $\gamma$ and martensitic $\varepsilon$ were antiferromagnetic, thus the presence of $\varepsilon$ was benign to MRI, which was a crucial requirement for a biomedical material.

Figure 4.5 - XRD spectrum of the sintered Fe-35Mn at different sintering temperatures and time.
4.3.3 Degradation (corrosion) behavior evaluation

4.3.3.1 Electrochemical analysis

Fig. 4.7 illustrates the open circuit potential (OCP) of the sintered Fe-35Mn alloy in 5% NaCl and SBF solution. The OCP in 5% NaCl was approximately -0.74V and -0.68V in SBF. Thus, the corrosion ability of Fe-35Mn alloy in 5% NaCl solution was stronger than that in SBF solution. As mentioned in Chapter 3 methodology, the Tafel analysis was carried out in the potential range around ±250mV from OCP vs SCE. Therefore, a range from -1.5V to 0 was selected to perform the polarization study.
Corrosion (degradation) current density is a key factor for evaluating the degradation performance [28]. The Tafel plots of the Fe-35Mn alloys samples produced by BE powder in 5% NaCl and SBF solutions are shown in Fig. 4.8 and Fig. 4.9 respectively. The corrosion potentials tested in the 5% NaCl solution was -0.73 to -0.90V, as compared to -1.0V for pure Fe in 3.5% NaCl solution [144]. When tested in the SBF solution, the corrosion potentials were approximately -0.70V to -0.87V, which was comparable with that of Fe-35Mn measured in the Hank’s solution (-0.74V reported in Ref. [3]).

Table 4.1 displays the degradation current density of each sample sintered under different sintering parameters. As can be seen, Fe-35Mn samples sintered at a higher temperature showed a slower electrochemical degradation, regardless of the sintering time (2 hours or 4 hours). Taking the 2-hour sintered samples corroded in 5% NaCl as an example, when the sintering temperature increased from 1000°C to 1200°C, the corrosion current density decreased from 267 to 170 μm/cm². Meanwhile, the corrosion rate decreased from 4.23 to 2.34 mmpy. In addition, when the samples sintered at the same temperature, the longer holding time led to a slower electrochemical degradation rate. For the samples sintered at 1200°C and corroded in 5% NaCl solution, the samples sintered for 2 hours, i.e. with
lower density, corroded faster than those sintered for 4 hours. The corrosion current densities of 1200°C sample sintered for 2 and 4 hours were 170 and 140μm/cm², which correspond to a corrosion rate of 4.23 and 1.77 mmpy respectively. These were expected because the increase of sintering temperature led to more densification.

Moreover, the samples degraded much faster in the 5 % NaCl solution than in SBF, as shown in Table 4.1 and Figs. 4.8 and 4.9. These results correspond to the OCP data (Fig. 4.7) that the 5% NaCl solution was more aggressive than SBF solution. It was clear that the degradation was largely dependent on the porosity in the Fe-Mn alloys, which was a result of the sintering parameters.

Figure 4.8 - Polarization curves of Fe-35Mn alloys sintered at different temperatures and time in 5 % NaCl solution.
Figure 4.9 - Polarization curve of Fe-35Mn alloys sintered at different temperatures and time in SBF solution.
Table 4.1 - Degradation rate of Fe-35Mn alloys in 5 % NaCl and SBF solutions calculated by Tafel plots.

<table>
<thead>
<tr>
<th>Sintering time (hour)</th>
<th>Sintering temperature (°C)</th>
<th>I_{corr} (μm/cm²) 5% NaCl</th>
<th>I_{corr} (μm/cm²) SBF</th>
<th>CR (mmpy) 5% NaCl</th>
<th>CR (mmpy) SBF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>2</td>
<td>267 ± 21</td>
<td>197 ± 16</td>
<td>4.23 ± 0.33</td>
<td>3.12 ± 0.22</td>
</tr>
<tr>
<td>1100</td>
<td>2</td>
<td>235 ± 38</td>
<td>174 ± 28</td>
<td>3.55 ± 0.31</td>
<td>2.63 ± 0.28</td>
</tr>
<tr>
<td>1200</td>
<td>2</td>
<td>170 ± 13</td>
<td>144 ± 21</td>
<td>2.34 ± 0.17</td>
<td>1.99 ± 0.28</td>
</tr>
<tr>
<td>1000</td>
<td>4</td>
<td>231 ± 45</td>
<td>170 ± 34</td>
<td>3.45 ± 0.55</td>
<td>2.54 ± 0.46</td>
</tr>
<tr>
<td>1100</td>
<td>4</td>
<td>195 ± 37</td>
<td>153 ± 34</td>
<td>2.83 ± 0.35</td>
<td>2.22 ± 0.29</td>
</tr>
<tr>
<td>1200</td>
<td>4</td>
<td>140 ± 30</td>
<td>116 ± 22</td>
<td>1.77 ± 0.24</td>
<td>1.46 ± 0.27</td>
</tr>
</tbody>
</table>

*I_{corr} - corrosion current density; CR - corrosion rate; mmpy – mm per year.

4.3.3.2 Static immersion test

The degradation rates obtained from the static immersion test in both 5% NaCl and SBF solutions are presented in Figs. 4.10 and 4.11. As with most metals, the degradation of the Fe-35Mn samples gradually slowed down over immersion time. This was related to the fact that the accumulation of the insoluble corrosion products on the alloy surface leads to a slowdown of the ion exchange between the substrate and solution. It was found that the samples sintered at 1200 °C for 4 hours with the highest density had the slowest degradation rate. On the other hand, samples sintered at 1000 °C, either sintered for 2 hours or for 4 hours corroded the fastest. This was caused by the large amount of the interconnected pores. Comparing with Figs. 4.10 and 4.11, it was clear that 5% NaCl solution was more aggressive than SBF that alloys produced at same condition degraded faster in 5% NaCl than in SBF.
Figure 4.10 - Degradation rates of Fe-35Mn alloys sintered at different temperatures and time in 5 % NaCl solution determined in static immersion tests.
4.3.4 Mechanical properties

Typical stress-strain curves for Fe-35Mn alloys sintered at various temperatures and time are illustrated in Fig. 4.12. The mechanical properties derived from such tests are presented in Table 4.2. Results indicated that the mechanical properties including the hardness, ultimate tensile strength (UTS) and ductility of sintered alloys were influenced by both sintering temperature and holding time.

In general, the mechanical properties increased with sintering temperature. For example, Fig. 4.12(b) shows the tensile curves sintered from 1000°C to 1200°C for 4 hours. When the sintering temperature increased from 1000 °C to 1200°C, the UTS of the sintered compacts increased from about 53.5 to 76.3 MPa and the strain increased from about 1.17...
to 1.46%, as well as the Rockwell hardness values (from about 30 to 43 HRH). This trend did not work very precisely in Fig. 4.12 (a) as the strains were almost the same (from about 0.9 to 1.2%). This reflected an insufficient diffusion bond between the particles, a consequence of short sintering time. It could also be seen that, with extending the holding time (comparing between Figs. 4.12(a) and (b)), the UTS and elongation increased as well. Taking samples sintered at 1200°C as an example, the longer sintering time led to a higher UTS, fracture strain and hardness: 76.3MPa, 1.46% and 43.00 for 4 hours sintering, in comparison with 50.7MPa, 1.11% and 33.78 for the case of 2 hours sintering.

Table 4.2 - Mechanical properties for Fe-35Mn compacts sintered at various temperatures and times

<table>
<thead>
<tr>
<th>Sintering time (hour)</th>
<th>Sintering temperature (°C)</th>
<th>Porosity (%)</th>
<th>Hardness HRH</th>
<th>UTS (MPa)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1000</td>
<td>35.84±0.41</td>
<td>28.52±2.93</td>
<td>41.1±3.62</td>
<td>1.12±0.11</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>32.71±0.91</td>
<td>30.3±2.11</td>
<td>49.7±3.01</td>
<td>0.86±0.08</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>26.98±0.40</td>
<td>33.78±2.25</td>
<td>50.7±4.21</td>
<td>1.11±0.15</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>31.97±1.29</td>
<td>30.23±0.91</td>
<td>53.5±2.98</td>
<td>1.17±0.09</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>29.84±0.93</td>
<td>31.53±1.52</td>
<td>60.3±4.60</td>
<td>1.25±0.12</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>19.43±0.99</td>
<td>43.00±2.26</td>
<td>76.3±4.17</td>
<td>1.46±0.12</td>
</tr>
</tbody>
</table>
Figure 4.12 - Tensile stress-strain curves of Fe-35Mn compacts sintered at various temperatures and times: (a) sintered at 1000°C, 1100°C and 1200°C for 2 hours, (b) for 4 hours.
Figure 4.13 - Fracture surfaces of the as-sintered Fe-35Mn alloys sintered at different temperature and holding time. (a) T=1000 °C, t=2hours, (c) T=1200 °C, t=2hours, (b) and (d), the close up image of (a) and (b).

Fig. 4.13 shows some typical microscopic fractography of alloys sintered at different temperatures and time after tensile testing. It could be seen that the sintered compacts exhibited some river pattern cleavage fractures, a characteristic of brittle fracture. As indicated in the closed up images (Figs. 4.13(b) and (d)), there were some small and shallow dimples (red arrows) on the fracture surface of those compacts which was the trace of the ductile fracture. These ductile dimples were observed on the grains in the dense area.

As shown in Fig. 4.13(c), the fracture surface in the crack region was smoother than that seen in image (a). Also seen in Figs.4.13(b) and (d), the surface of sample sintered at
1200°C (Fig.4.13 (d)) showed more shallow dimples than that of 1000 °C sample (Fig.4.13(b)). This should be due to that fact that the sample sintered at 1200 °C had lower porosity and smaller pore size than the one sintered at 1000 °C. This will be summarised in Section 4.4.

From the above presented results, it could be concluded that all sintered compacts exhibited a typical brittle failure while some ductile fracture occurring in some specific areas. Powder detachment was the main rupture mechanism as a result of the weak particle bonding due to the insufficient diffusion.

4.4 Summary

Fe-35Mn alloys were produced by a simple blend-press-sinter method in this chapter. The effects of sintering temperature and holding time on the microstructure evolution, densification, corrosion behavior as well as mechanical properties of the sintered Fe-35Mn compacts were studied. The following conclusion can be drawn:

- With increasing the sintering temperature and holding time, the porosity level of the sintered compacts decreased. This was closely related to the powder densification – a diffusion controlled process.
- The main phases present in the sintered samples were austenitic $\gamma$ and martensitic $\epsilon$, which could be beneficial to the magnetic resonance imaging (MRI) compatibility due to their anti-ferromagnetic property. The variation of sintering temperature and time did not influence the phase.
- Potentio-dynamic analysis revealed a degradation rate ranging from about 1.5 to 4mmpy in both 5% NaCl and SBF solutions, which met the degradation requirement with a 6 ~ 12 months service life for a biodegradable material.
- The static immersion testing showed the real corrosion process. The overall corrosion rate decreased while extending the exposed time.
- The mechanical properties including tensile strength, ductility and hardness were related to the porosity and densification.
- The fracture mechanism of Fe-35Mn compacts sintered under different conditions showed a dominant brittle fracture.
Chapter 5 Powder Sintering from Mechanically Milled (MMed) Powder

5.1 Introduction

In Chapter 4, Fe-35wt.%Mn alloys fabricated by blended elemental (BE) powders via powder sintering method were reported. Various sintering temperatures and holding times were investigated in terms of their effects on powder densification, microstructure and mechanical properties. It is believed that shortening the solid-state diffusion path can accelerate the powder densification. In this sense, a mechanical milling (MMing) technique is proposed to refine the powder size and shorten the diffusion distance.

MMing is a powder preparation technique which has been developed in the last two decades [145, 146]. In MMing process, long-time vigorous shock and collision from the milling media to powder particles are involved. Repeating deformation and breakage, welding together between the mix powder particles and mutual diffusion and solid-state reaction between atoms may happen in this MMing process [147]. The objectives of MMing are to reduce the particle size and change particle shape, to mix and blend and to synthetize nanocomposite [145, 148]. In certain cases, mechanical alloying-MAing (i.e. forming solid solution) could be achieved during milling process, depending on the nature of powder mixtures.

In this chapter we selected a MMing method to modify the starting powders, aiming to obtain finer powder mixture, and if possible, pre-alloyed or pre-solid-state-diffused powders. A series of MMing conditions were selected in order to determine optimum parameters for future powder preparation. After MMing various compacting pressures and methods were used to consolidate the powders. After sintering, the porosity, microstructure, mechanical properties and corrosion resistance of the mechanically milled (MMed) Fe-35Mn alloys were investigated.
5.2 Processing

Elemental iron and manganese powders were mixed at a nominal composition of Fe-35Mn. The powder blend was subjected to ball milling for 2, 4, 6, 12 and 20 hours with a ball-to-powder (B-P) ratio of 2:1, 5:1 and 10:1. An amount of 0.5 wt% stearic acid was added as processing control agent (PCA) during ball milling.

Generally, a better MMing effect will be promoted by a more randomly collision using milling balls in multiple sizes than balls in single size. In this work, stainless steel balls in three different sizes were employed to conduct the MMing process. The detailed parameters of milling balls are listed in Table 5.1. φ18mm balls and φ10mm balls were to break the powder particles and φ6mm balls were generally for further grinding and refining.

Table 5.1 - The parameters of milling balls.

<table>
<thead>
<tr>
<th>Ball diameter (mm)</th>
<th>Ball mass (g)</th>
<th>Number of balls</th>
<th>Total mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>24.70</td>
<td>3</td>
<td>74.1</td>
</tr>
<tr>
<td>10</td>
<td>4.14</td>
<td>18</td>
<td>74.52</td>
</tr>
<tr>
<td>6</td>
<td>0.89</td>
<td>114</td>
<td>101.46</td>
</tr>
</tbody>
</table>

Phase constituent (XRD, Siemens D5000) and optical microscopic imaging were used to monitor any new phase formation and the particle refinement during milling. The final as-milled powder (produced under the chosen MMing condition) was uni-axially pressed under 200, 400 and 600 MPa into pellets 12 mm in diameter. The attendant thickness of the pellets was 5.5 to 6.2 mm. One batch of these pellets was further densified with cold isostatic pressing (CIPing) under a pressure of 200 MPa.

All pellets were sintered in a tube furnace at 950° in a nitrogen atmosphere for 8 hours. The sintering cycle of the MMed compacts is presented in Fig. 5.1. Minor oxidation was found on the surfaces of the sintered samples and the surface oxide layer was removed for the sequent evaluation.
Vickers micro-hardness was measured with a micro-hardness tester. The load used was 50 gf and dwell time was 30 seconds. At least 7 readings were made and the average value was used as the reported hardness.

Electrochemical impedance spectroscopy (EIS) were reported in this chapter. The detailed experimental procedure was introduced in Chapter 3. EIS is considered as a very useful and valuable tool for studying both the electrochemical reactions and the bulk transport properties of a material on its surface [149-151]. Typically, EIS measurements are performed over a wide range of frequencies (several milli-hertz to several mega-hertz). Usually, equivalent circuits involving simple components are simulated by the interpretation of the resulting spectra. Some typical circuit components are resistors, capacitors, inductors and constant phase element (CPE).

![Sintering profile of producing Fe-35Mn alloys from MMed powder in tube furnace under nitrogen atmosphere.](image)

Figure 5.1 - Sintering profile of producing Fe-35Mn alloys from MMed powder in tube furnace under nitrogen atmosphere.
5.3 Results and discussion

5.3.1 Powder preparation by mechanical ball milling

Fig. 5.2 shows the optical microscopic images of pre-blended Fe-Mn powder. As shown, the size of starting powders ranged from about 20 to 60μm. The optical microscopic pictures of the Fe-Mn powder after MMing at different B-P ratios and times are presented in Fig. 5.3.

Generally, powder will be uniformly distributed and particles are finer after MMing under all milling conditions. Comparing the optical micro-images in the first column, the B-P ratio 2:1 had not produced enough energy to reduce the particle size – the difference of particle size was not very obvious. The powder particles of the blended powder had been significantly decreased down to less than 10μm under the B-P ratio of 5:1 and 10:1, especially for the 10:1 ratio the particle size almost reached nano level.

Usually, the longer milling time leads to much finer particles. However, when the milling time was extended from 6 hours to 12 hour at the ratio 5:1, some larger particles appeared. This phenomenon happened much earlier at 10:1 ratio that the nano-sized powders agglomerated or rebounded from 4 hours milling as shown in Fig. 5.3 (l). Fig. 5.4 shows an enlarged image of Fig. 5.3 (l). It showed that there were some tiny particles attached on the larger particle surfaces, indicating that the presence of larger particles was caused by the reunion of smaller particles.

Figure 5.2 - (a) and (b) Optical microscopic images of pre-blended Fe-Mn powder mixture at different magnifications.
Figure 5.3 - Optical microscopic pictures of Fe-Mn powder after MMing at different B-P ratio and times: (a) 2:1, 2h, (b) 2:1, 4h, (c) 2:1, 6h, (d) 2:1, 12h, (e) 2:1, 20h, (f) 5:1, 2h, (g) 5:1, 4h, (h) 5:1, 6h, (i) 5:1, 12h, (j) 5:1, 20h, (k) 10:1, 2h, (l) 10:1, 4h, (m) 10:1, 6h, (n) 10:1, 12h, (o) 10:1, 20h,
Fig. 5.5 displays the XRD pattern of the MMed Fe-Mn powder mixture under different milling conditions, comparing with the spectra of pre-blended Fe-Mn powder mixture and the spectra of Fe-35Mn sample reported in Chapter 4. As shown, no shifts were found from the peaks obtained under all milling conditions comparing with the pre-blended powder. This indicated that no phase change happened during M Ming.

By comparing between the spectra under the same B-P ratio but different milling time, all the \( \alpha \)-Mn peaks became shorter and wider with increasing the milling time. It occurred more severely at 5:1 and 10:1 B-P ratios. The broadening of the Mn peaks indicated that the particle refinement had occurred. It was apparent that with a higher B-P ratio the particle refinement was readily achieved. The gradual disappearance of Mn peaks also implied that Mn had diffused, or at least partially diffused, into Fe matrix.
Figure 5.5 - XRD on MMed powder at different B-P ratios for various milling times: (a) B-P ratio=2:1, (b) B-P ratio=5:1 and (c) B-P ratio=10:1.
Overall, diffusion started to take place during MMing process, as evidenced in the XRD spectra Fig. 5.5. Partially Mn had dissolved into Fe but not enough for phase change. This partial diffusion was believed to promote the subsequent sintering process.

From the above consideration of the particle size and XRD spectra, a B-P ratio of 5:1 and a milling time of 6 hours were determined as the optimum milling parameters. The ESEM images of pre-blended and final milled powder are present in Fig. 5.6. Particle sizes of final MMed powder ranged from 5 to 30μm. The Fe-35Mn alloys were further sintered from the powder that was MMed for 6 hours at a B-P ratio of 5:1, and the results were presented in the following sections.

Figure 5.6 - ESEM images of Fe-Mn mixed powder (a) before and (b) after ball milling. Milling conditions: 6 hours, 5:1 B-P ratio.
5.3.2 Density, porosity, phase constituents and microstructure

Fig. 5.7 shows the porosity of the sintered Fe-35Mn compacts, which were pressed at different pressures and with a further CIPing at 200 MPa. As expected, a higher compaction pressure resulted in a lower porosity. Porosity of un-CIPed samples were ranging from 12.1 to 7.8% when the compaction pressure increased from 200MPa to 600MPa. CIPing could further densify the compacts and hence increase the sintered density as shown in Fig. 5.7. The porosity had been levelled down to about 6.5 to 8.1% by CIPing.

Comparing with the results of the samples produced from BE in Chapter 4, the samples produced from MMed powder presented a higher densification level. This was mainly due to the finer starting powder and the shorter diffusion distance between the particles. The refined microstructure in the MMed particles was beneficial to promote the densification of Fe-35Mn powder in the current study. Moreover, the achievement of the pre-diffusion in MMing before sintering was also able to accelerate the final densification.

![Figure 5.7 - Porosity of un-CIPed and CIPed Fe-35Mn alloys](image-url)
ESEM micro-images of the sintered samples are displayed in Fig. 5.8, which further present the densification of all the sintered compacts. Figs. 5.8 (a), (c) and (e) show the microstructures of the un-CIPed sample surfaces. Figs. 5.8 (b), (d) and (f) in the right column illustrate the microscopic images of the sample with additional CIPing process. As illustrated, less pores (black) existed in the CIPed samples. Fig. 5.9 further demonstrates a close-up image of Fig. 5.8 (f).

Fig. 5.9 presents a close-up image of the sample sintered from the powder compact that was pressed at 600MPa and then CIPed at 200 MPa. As shown in Fig. 5.9, the pores in this sample were close to micro-pores, only about 1 to 7μm in diameter. This might be caused by the unbalanced diffusion between Mn and Fe, a typical Kirkendall effect [152].

The XRD pattern of the sintered Fe-35Mn alloy is presented in Fig. 5.10. Three phases were identified: austenitic γ, martensitic ε and α′, with γ being the main phase. As per the Fe-Mn binary phase diagram [141], at room temperature (RT) only γ-phase exists for the Fe-35Mn composition [141]. It has been reported that in Fe-Mn alloys with less than 10% Mn, only the martensitic α′ phase (BCC) exists at RT. In the alloys with Mn content between 10 and 15 wt%, another martensitic ε phase also occurs at RT [141]. The presence of martensitic ε and α′ in the Fe-35Mn alloy in this study was deemed to be attributed to some local compositional inhomogeneity in the sintered sample. The formation of such phases had been discussed in Chapter 4. Although α′ phase was ferromagnetic, the minor presence of this phase would not have a significant influence on the magnetic property of the bulk sample, because γ and ε phases were anti-ferromagnetic.
Figure 5.8 - ESEM images of the polished samples sintered from the powder compacts under different compaction pressures and methods: (a) 200MPa, un-CIPed, (b) 200MPa, CIPed, (c) 400MPa, un-CIPed, (d) 400MPa, CIPed, (e) 600MPa, un-CIPed and (f) 600MPa, CIPed.
Figure 5.9 - A zoom in image of 600MPa CIPed sample (Figure 5.8 (f)).

Figure 5.10 - XRD pattern of the sintered Fe-35Mn alloy
5.3.3 Degradation (corrosion) behavior evaluation

5.3.3.1 Electrochemical analysis

Potentiodynamic polarization was performed on the sintered Fe-35Mn alloys in 5% NaCl and SBF solutions. Representative polarization curves for the samples with processing conditions of die-pressing and die-pressing-then-CIPing are shown in Figs. 5.11 and 5.12. The corrosion potential of the Fe-35Mn tested in 5% NaCl was approximately -0.678V and in SBF was from -0.624V to -0.745V, which was comparable with that of the Fe-35Mn measured in Hank’s solution: -0.74V reported in Ref. [3].

The average electrochemical parameters and corrosion rates calculated for the present Fe-Mn alloys are listed in Table 5.2. Fig. 5.13 further summarised how porosity was related to the corrosion current density and corrosion rate of the samples in 5% NaCl and SBF solutions. Results showed that with the increase of densification the corrosion current density and corrosion rate decreased. For example in the un-CIPed samples, the corrosion current density and corrosion rate in 5% NaCl solution dropped from about 104μA and 1.4 mmpy to 74μA and 1.0 mmpy if the compaction pressure increased from 200MPa to 600MPa. Moreover with the additional CIPing treatment, the densification of the samples had been enhanced. This led to a slower corrosion rate as shown in Table 5.2 and Fig. 5.13. For instance, in 5% NaCl solution, the corrosion rate of the sample made from the powder compact at 200MPa decreased from about 1.4 to 1.1 mmpy. Furthermore, comparing between samples corroded in different corrosive media, it was found that SBF was less corrosive than 5%NaCl solution.
The fully solid Fe-35Mn alloys had shown a corrosion rate of 0.4 to 0.7 mmpy [15]. The Fe-35Mn alloys produced from the MMed powder corroded faster. This was simply because of the presence of tiny pores in this study. The corrosion rate of the less-dense Fe-35Mn alloys in this study reached 1.4 mm/year that was about twice as high as the cold rolled Fe-35Mn alloys and electroformed iron, and eight times high as annealed CTT-Fe (casting and thermo-mechanical treatment) [54]. Also this value was about half of the rate for AM60B Mg alloys [54]. The achievement of this moderate corrosion rate was encouraging.

Table 5.2 Degradation rate of Fe-35Mn alloys in 5% NaCl and SBF solutions calculated by Tafel plots.

<table>
<thead>
<tr>
<th>Compaction pressure (MPa)</th>
<th>$I_{corr}$ (μA/cm²)</th>
<th>CR (mmpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5% NaCl</td>
<td>SBF</td>
</tr>
<tr>
<td>Un-CIPed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200MPa</td>
<td>103.5±10.0</td>
<td>92.0±9.6</td>
</tr>
<tr>
<td>400MPa</td>
<td>82.5±9.9</td>
<td>75.5±9.6</td>
</tr>
<tr>
<td>600MPa</td>
<td>73.8±11.2</td>
<td>58.3±7.9</td>
</tr>
<tr>
<td>CIPed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200MPa</td>
<td>82.1±9.6</td>
<td>73.3±8.7</td>
</tr>
<tr>
<td>400MPa</td>
<td>74.7±4.2</td>
<td>62.5±4.1</td>
</tr>
<tr>
<td>600MPa</td>
<td>69.0±5.6</td>
<td>49.2±5.2</td>
</tr>
</tbody>
</table>

* $I_{corr}$ - corrosion current density; CR - corrosion rate; mmpy - mm per year.
Figure 5.11 - Polarization curves of un-CIPed Fe-35Mn alloys (a) in 5% NaCl and (b) SBF solutions.
Figure 5.12 - Polarization curves of CIPed Fe-35Mn alloys (a) in 5% NaCl and (b) SBF solutions.
Figure 5.13 - Relationship among current density, porosity and corrosion rate (CR), (a) in 5% NaCl and (b) in SBF solution.
Fig. 5.14 shows the Nyquist plot of EIS performed at open circuit potential (OCP) of the Fe-35Mn sintered compact, which was pressed at 400MPa with post CIPing. The EIS tests were conducted in both 5% NaCl and SBF media. Each plot consisted of two capacitive semicircle loops at high and medium frequency. The high frequency loop was related to the process of deposition of corrosion products. The medium frequency capacitive loop was attributed to mass transport of the corrosion process of the bulk metal due to the growth of the corrosion product layer. At low frequencies (on the right side of each plot), the spectra obtained from 5% NaCl solution appeared an inductive loop. This meant the corrosion of Fe-35Mn alloy in 5% NaCl solution started with the occurrence of relaxation processes of adsorbed species such as Fe(OH)$_2$ or Fe(OH)$_3$. A straight line appeared in low frequency range in the spectra obtained from SBF solution. The straight line with about 45° slope was ascribed to the Warburg diffusion. It meant that, in the initial period of immersion, the corrosion process of Fe-Mn alloy in SBF was controlled by both diffusion and electrochemical polarization mechanisms.

Figure 5.14 - Typical Nyquist plots of Fe-35Mn alloy produced from powder compact that was pressed at 400MPa and CIP compaction. The EIS tests were performed in both 5% NaCl and SBF solutions under OCP.
The most properly fitted circuits and their values in both testing solutions are shown in Figs.5.15 (a) and (b). Circuit simulated by plot obtained from 5% NaCl solution is shown in Figs. 5.15 (a), which consisted of various components where Rs, CPE, Rt, Ca, Ra, Lf and Rf indicated the solution resistance, capacitance double layer in constant phase element form, corrosion products layer resistance, double-layer capacitance, charge transfer resistance, inductance and inductance resistance. Circuit simulated by plot obtained from SBF solution showing in Fig. 5.15 (b) consisted of Rs, Cd, Rt, Ca, Ra and W where W represented Warburg impedance.

Figure 5.15 - The equivalent circuit of EIS spectra obtained under OCP for the Fe-Mn alloy produced from powder compact that was pressed at 400MPa and CIP compaction. The EIS tests were performed in (a) 5% NaCl and (b) SBF solutions.
The calculated data from the equivalent circuits are listed in Tables 5.3 and 5.4. It was evident from these two tables that the Rs of SBF was much higher than that of 5% NaCl solution. The higher solution resistance led to the lower corrosive ability. Both Rt (demonstrating the corrosion product layer formation ability) and Ra (demonstrating the charge transfer ability between bulk metal and solution) in SBF were significantly higher than that in 5% NaCl. Rt in SBF was 13.8, almost doubled the value in 5% NaCl solution (8.48). Ra in SBF was 26.85, again two times higher than the value in 5% NaCl solution (13.29). It indicated that the initial corrosion of Fe-Mn alloy in SBF was harder to proceed than in 5% NaCl as well as the later corrosion layer formation stage. As shown in Fig. 5.14, the loops in SBF had larger circles than those obtained in 5% NaCl, which showed an agreement with the calculated data from simulated circuit. The results also corresponded to prior polarization results that sample corroded slower in SBF than in 5% NaCl solution.
Table 5.3 - Fitting results of equivalent circuit for Fe-35Mn alloy produced at 400MPa and CIP compaction in 5% NaCl under OCP

<table>
<thead>
<tr>
<th>Solution</th>
<th>Rs (ohm-cm²)</th>
<th>CPE, Yo (S-secⁿ/cm²)</th>
<th>n</th>
<th>Rt (ohm-cm²)</th>
<th>Ca (F/cm²)</th>
<th>Ra (ohm-cm²)</th>
<th>Lf (Henri-cm²)</th>
<th>Rf (ohm-cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%NaCl</td>
<td>0.49</td>
<td>1.27</td>
<td>0.93</td>
<td>8.48</td>
<td>4.04 E-4</td>
<td>13.29</td>
<td>8.71</td>
<td>1.00 E-2</td>
</tr>
<tr>
<td>Error</td>
<td>3.12</td>
<td>6.25</td>
<td>2.12</td>
<td>3.80</td>
<td>4.84</td>
<td>1.81</td>
<td>1.76</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Table 5.4 - Fitting results of equivalent circuit for Fe-35Mn alloy produced at 400MPa and CIP compaction in SBF solution under OCP

<table>
<thead>
<tr>
<th>Solution</th>
<th>Rs (ohm-cm²)</th>
<th>Cd (F/cm²)</th>
<th>Rt (ohm-cm²)</th>
<th>Ca (F/cm²)</th>
<th>Ra (ohm-cm²)</th>
<th>Warburg, Yo (S-secⁿ/5/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBF</td>
<td>24.13</td>
<td>2.20 E-5</td>
<td>13.8</td>
<td>2.40 E-4</td>
<td>26.85</td>
<td>6.51 E-2</td>
</tr>
<tr>
<td>Error</td>
<td>1.90</td>
<td>4.21</td>
<td>3.85</td>
<td>4.62</td>
<td>6.72</td>
<td>3.24</td>
</tr>
</tbody>
</table>
Fig. 5.16 compares the Nyquist plots of the Fe-35Mn sintered compacts that were pressed at 400MPa and 600MPa with an additional CIPing. The EIS tests were performed in 5% NaCl solution. Results showed that the 600MPa CIPed sample presented a similar EIS spectra as 400MPa CIPed sample, but the sizes of both two loops were bigger than that in the latter sample. Both samples possessed the same impedance phenomenology and the same simulated circuit as shown in Fig. 5.15 (a).

The calculated data of these two samples from equivalent circuit displayed in Fig. 5.15 (a) are listed in Table 5.5. The two samples had similar Rt: 8.48 for 400MPa CIPed sample and 9.10 for 600MPa CIPed sample but very different Ra: 13.29 for 400MPa CIPed sample and 25.8 for 600MPa CIPed sample. The difference in Ra was more dominant. This indicated that more charge transfer happened between metal and corrosive media of the 400MPa CIPed sample than the 600MPa CIPed sample. This might be caused by the higher exposed corrosion area in the 400MPa CIPed sample since it showed a higher porosity than the 600MPa CIPed sample (refer to Section 5.3.2).
Table 5.5 - Fitting results of equivalent circuit for Fe-35Mn alloy in 5% NaCl. The sintered samples were made from the powder compacts at 400MPa and CIP compaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rs</th>
<th>CPE, Yo</th>
<th>n</th>
<th>Rt</th>
<th>Ca</th>
<th>Ra</th>
<th>Lf</th>
<th>Rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIPed-400MPa</td>
<td>0.49</td>
<td>1.27</td>
<td>0.93</td>
<td>8.48</td>
<td>4.04 E-4</td>
<td>13.29</td>
<td>8.71</td>
<td>1.00 E-2</td>
</tr>
<tr>
<td>Error</td>
<td>3.12</td>
<td>6.25</td>
<td>2.12</td>
<td>3.80</td>
<td>4.84</td>
<td>1.81</td>
<td>1.76</td>
<td>1.40</td>
</tr>
<tr>
<td>CIPed-600MPa</td>
<td>0.46</td>
<td>1.20 E-5</td>
<td>0.94</td>
<td>9.10</td>
<td>3.64 E-4</td>
<td>25.8</td>
<td>179.8</td>
<td>26.17</td>
</tr>
<tr>
<td>Error</td>
<td>7.26</td>
<td>5.12</td>
<td>2.07</td>
<td>3.28</td>
<td>4.50</td>
<td>1.94</td>
<td>8.25</td>
<td>2.25</td>
</tr>
</tbody>
</table>
Figure 5.16 - Typical Nyquist plots of Fe-35Mn alloy produced under 400MPa and 600MPa compaction with CIPing in 5\% NaCl solution under OCP.

Fig. 5.17 shows the Nyquist impedance diagrams of the Fe-35Mn samples in 5\% NaCl solution obtained at different external voltages, in comparison with the EIS performed at OCP. When it was tested under OCP, the sample self-corroded in corrosive media. Two semicircles at medium and high frequency appeared which represented the process of bulk alloys corrosion and corrosion products layer formation. When external voltages (+0.2 and +0.5V vs OCP) were applied, the small semicircle at high frequency range disappeared and the semicircle at medium frequency shrank. The increased external voltage applied led to a more drastic charge transfer. No corrosion product layer was formed during this process while the bulk alloy was completely exposed to the corrosive media.
5.3.3.2 Static immersion test

Fig. 5.18 shows the degradation rate obtained from the immersion test. Like most metals, the degradation gradually slowed down with the immersion time. Samples after CIPing corroded slower than those just compressed by uni-axial die compaction. This result was in good agreement with the electrochemical corrosion data demonstrated in Section 5.3.3.1.

During immersion, the solutions became semi-transparent or opaque with some orange colour insoluble substances suspending in the solutions. On the sample surface were dark black pasty-like corrosion products. These corrosion products were identified using XRD analysis. As shown in Fig. 5.19, the main phases of the corrosion products were mainly composed of iron oxides, manganese oxides, ferric hydroxides and goethite (FeO(OH)). Some phosphates appeared in Fig. 5.19, such as Mg₃(PO₄)₂·2H₂O. Fig. 5.19 also showed some amorphous phase with very low intensity; they might be some hydrated degradation products [12].

Figure 5.17 - Typical Nyquist plots of Fe-35Mn alloy produced under 400MPa and CIPing compaction in 5% NaCl solution at different external voltages: OCP, +0.2V vs OCP and +0.5V vs OCP.
Figure 5.18 - Corrosion rate- time relationship of Fe-35Mn alloys produced under different compaction condition in different testing solutions: (a) un-CIPed in 5% NaCl solution, (b) CIPed in 5% NaCl solution, (c) un-CIPed in SBF solution and (d) CIPed in SBF solution.
5.3.4 Mechanical properties

The typical stress vs. strain curves for the sintered Fe-35Mn alloys produced from MMed powders are presented in Figs. 5.20 (a) and (b). The relationship between compaction pressure/methods and mechanical properties of all studied alloys are summarised in Table 5.6.

Fig. 5.20 (a) compares the tensile curves of the samples pressed at different pressure ranging from 200 to 600 MPa. All of these samples were subjected to CIPing. It could be seen that with increasing the compaction pressure, the hardness, ultimate tensile strength (UTS) and ductility were increased. The sample compacted under 600MPa had the highest values amongst others. They reached 281HV, 240MPa and 2.82%, respectively. Fig. 5.20 (b) presented the effect of CIPing; all the samples were pressed at 600MPa. As shown in Fig.5.20 (b), the samples after CIPing presented higher mechanical properties as compared to those samples that were not CIPed (200HV, 223MPa and 1.90%).

Fig. 5.21 shows the relationship between porosity and hardness of the sintered Fe-35Mn alloys. As expected, a higher compaction pressure resulted in a lower porosity. CIPing could further densify the compacts and hence increase the sintered density. Consequently, a less dense Fe-35Mn sample demonstrated a lower hardness value.
Figure 5.20 - Typical stress-strain curves for sintered Fe-35Mn alloys compacted under different pressures and methods.
Table 5.6 - Tensile properties of Fe-Mn alloys sintered from powder compacts that were pressed at different compaction pressure and with or without CIPing.

<table>
<thead>
<tr>
<th>Compaction pressure (MPa)</th>
<th>Porosity (%)</th>
<th>Hardness (HV)</th>
<th>UTS (MPa)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-CIPed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>12.1±1.1</td>
<td>105±5.6</td>
<td>190±10.1</td>
<td>1.62±0.14</td>
</tr>
<tr>
<td>400</td>
<td>11.0±1.5</td>
<td>175±8.1</td>
<td>206±8.4</td>
<td>1.62±0.17</td>
</tr>
<tr>
<td>600</td>
<td>7.8±1.1</td>
<td>200±6.1</td>
<td>223±6.8</td>
<td>1.90±0.20</td>
</tr>
<tr>
<td>CIPed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>8.1±0.9</td>
<td>112±4.2</td>
<td>225±12.1</td>
<td>1.66±0.15</td>
</tr>
<tr>
<td>400</td>
<td>7.0±0.5</td>
<td>232±8.5</td>
<td>230±9.5</td>
<td>2.68±0.26</td>
</tr>
<tr>
<td>600</td>
<td>6.52±0.6</td>
<td>281±18.2</td>
<td>240±9.2</td>
<td>2.92±0.21</td>
</tr>
</tbody>
</table>

Figure 5.21 - Relationship between hardness and porosity of Fe-35Mn alloys
A typical microscopic fracture surface of the sintered Fe-35Mn alloys produced from the MMed powders is displayed in Fig. 5.22 (a). A zoom in image is also presented in Fig. 5.22 (b). Many areas of the fracture surface of the specimen revealed a ductile rupture. Powder detachment was still the main fracture mode like the samples produced from BE powder (Chapter 4). Inefficient bonding strength between particles at this stage led to some particles being pulled out by the tension force. However, there were also occasional features of ductile fracture as evidenced by some dimples appearing. Mixed mode fracture was consistent with the fracto-graphic features for the Fe-35Mn alloys produced by powder metallurgic (PM) route. The specimens were always not fully dense; crevices and pores in the sintered compacts would lead to an early fracture.

Figure 5.22 - Fracture surfaces of the as-sintered Fe-Mn alloys sintered at (a) 200MPa-pressed-CIPed sample and (b) at higher magnification.
5.4 Summary

In this study, a series of MMing conditions were carried out. After MMing, various compacting pressures and CIPing were conducted to produce Fe-35Mn powder, prior to sintering. The porosity, microstructure, the mechanical properties and corrosion behaviour of the sintered Fe-35Mn alloys were investigated. The following conclusions can be drawn.

- With increasing the B-P ratio and milling time, the particle size decreased. During MMing partial diffusion of Mn into Fe particles occurred,
- A higher compaction pressure resulted in a lower porosity level. CIPing further enhanced the samples’ densification.
- XRD results of the sintered Fe-35Mn alloys showed that anti-ferromagnetic austenitic $\gamma$ and martensitic $\varepsilon$ were the main phase. The minor presence of ferro-magnetic $\alpha'$ would not influence the MRI compatibility.
- When compared with the results in Chapter 4, the sintered Fe-35Mn alloy demonstrated a slightly slower degradation rate but higher than fully solid Fe-35Mn alloys reported in the literature. A higher porosity resulted in a higher degradation rate. The degradation rate in SBF was slightly slower than in 5% NaCl solution. All samples, with porosity being from 6.5% to 12.2%, revealed a degradation rate from 0.6 to 1.4 mm/year.
- EIS tests were conducted and fitting equivalent circuits were obtained to simulate the corrosion process of Fe-35Mn alloy. Alloy with higher density revealed to higher impedance. Sample corroded in SBF presented higher impedance than in 5% NaCl solution. These results were in good agreement with potentiodynamic polarization results and immersion corrosion results.
- Samples fabricated in this chapter showed better mechanical properties than those made from BE powder (in Chapter 4). The UTS ranged from 190 to 240 MPa. The fractographic study showed that more dimples were observed in the samples, although the fracture mechanism was mixture of ductile and brittle rupture.
Chapter 6 Porous Fe-35wt.%Mn Produced via Sintering from NH₄HCO₃ Porogen

6.1 Introduction

Some dense Fe-35wt.%Mn alloys had been produced using powder metallurgical (PM) methods, followed by cold rolling or quenching process and showed satisfactory tensile properties (yield strength, ultimate tensile strength (UTS) and elongation), as compared with stainless steel [3]. However, the corrosion rate of such dense alloys was slower than required, only 0.4 to 0.7 mmpy [15]. A straightforward approach to speed up the degradation rate is to enlarge the exposed area of materials to corrosion environment. Adding pores using space holding materials through PM technique is a way to achieve this objective.

Pores, in particular, interconnected open-cell pores would produce a larger surface area. These interconnected pores would allow the testing solution flowing to the inner part of testing material, which means more reaction area would be generated. Desired shape and size of the pores and morphology of the porous structure can be readily controlled by the selected space holding material, often termed ‘porogen’ [153]. The most popular porogen materials are ammonium bicarbonate particles (NH₄HCO₃) [111, 153, 154], polymethyl methacrylate (PMMA) [155], poly-L-lactic acid (PLLA) [156] and NaCl particles [157]. The porogen particles which can be removed by thermal treatment at low temperatures, such as NH₄HCO₃ with relatively low melting/dissociation temperature, become a good candidate for Fe-based alloys.

In this chapter, firstly, porous Fe-35Mn alloy foam samples were fabricated through the use of NH₄HCO₃ particles as porogen. For comparison purpose, a batch of blended elemental (BE) Fe-35Mn samples was also produced by a simple blend-press-sinter process. The microstructure and the degradation characteristics of the porous Fe-35Mn alloy samples having varying degrees of porosities were investigated.
6.2 Processing

6.2.1 Powder mixing and compaction

Elemental iron and manganese powders at a nominal composition of Fe-35Mn were mixed in a rotary blender for 10 hours. One third of this powder mixture was used for making Fe-35Mn compacts without NH₄HCO₃ while the other two thirds were further mixed with 10 vol.% or 20 vol.% NH₄HCO₃.

NH₄HCO₃ has a density of 1.586 g/cm³, melting temperature of 41.9 °C, 315 K and non-solubility in methanol. It decomposes above about 36 °C into ammonia, carbon dioxide and water. In this study, the NH₄HCO₃-containing powder mixtures were mixed in the planetary ball mill machine for 1 hour. Ethanol (2vol.%) was sprayed on NH₄HCO₃ particles before mixing stage to obtain a sticky surface for the adhesion of NH₄HCO₃ particles with iron and manganese particles. This promoted uniform distribution of Fe-Mn powder over NH₄HCO₃ nodules. The BE powder mixtures and the NH₄HCO₃-containing (10 vol.% and 20 vol.%) mixtures were uni-axially pressed under 400MPa into pellets 16 mm in diameter and 4 to 5mm thick.

6.2.2 Sintering

The NH₄HCO₃-containing pellets were first placed in a tube furnace under a nitrogen atmosphere for thermal debinding processing. The space holder removal process is listed below in Table 6.1. After thermal debinding, all pellets including the pellets without any NH₄HCO₃ were sintered in a vacuum furnace at 1200°C for 2 hours, with a heating rate of 10°C/min. The entire processing of sample preparation is shown in Fig. 6.1.
Table 6.1 - Thermal debinding process for space holder removal.

<table>
<thead>
<tr>
<th>Temperature range (ºC)</th>
<th>Rate (ºC/min)</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0~120</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>120</td>
<td>Hold</td>
<td>60</td>
</tr>
<tr>
<td>121~300</td>
<td>5</td>
<td>36</td>
</tr>
<tr>
<td>300</td>
<td>Hold</td>
<td>120</td>
</tr>
</tbody>
</table>

Figure 6.1 - The flow chart of the entire processing diagram.
6.3 Results and discussion

6.3.1 Density and porosity

The total (overall) porosity and open-cell porosity data of the sintered Fe-35Mn alloys are listed in Table 6.2. As expected, addition of NH$_4$HCO$_3$ particles significantly increases the porosity in the sintered compacts. For instance, the total porosity in the compact with 20 vol.% NH$_4$HCO$_3$ addition was 48% and most of the pores were open-cell pores. In contrast, without addition of NH$_4$HCO$_3$, the porosity was much lower and the majority was close pores. The fraction of open-cell porosity in the compacts is illustrated in Fig. 6.2, as a function of the total porosity in the compacts produced with different volumes of spacer addition. A positive linear relationship is observed between the open porosity fraction and total porosity for the sintered compacts. It can be seen that the highest open-cell porosity fraction was observed in the compact with addition of 20 vol.% NH$_4$HCO$_3$ particles; the open-cell porosity amounts for ca. 70% of total porosity. In the compact without spacer addition, the open-cell porosity amounts for ~30% of the total porosity.

Table 6.2 - Total porosity, open-cell porosity values and pore size analysis on the prepared Fe$_{35}$Mn alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total porosity (%)</th>
<th>Open-cell porosity (%)</th>
<th>Mean pore size (µm)</th>
<th>Maximum pore size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With no spacer</td>
<td>27.3 ±0.6</td>
<td>9.7±1.2</td>
<td>7±2</td>
<td>55±12</td>
</tr>
<tr>
<td>10 vol.% spacer</td>
<td>40.0 ± 3.9</td>
<td>25.4±1.2</td>
<td>31±5</td>
<td>134±20</td>
</tr>
<tr>
<td>20 vol.% spacer</td>
<td>48.2 ± 0.3</td>
<td>31.1±1.8</td>
<td>55±7</td>
<td>355±51</td>
</tr>
</tbody>
</table>
6.3.2 Phase constituents and microstructure

All sintered Fe-35Mn specimens were composed of a main austenitic $\gamma$ phase (f.c.c.) with a minor martensitic $\varepsilon$ phase (c.p.h.), as shown in a typical XRD pattern (Fig. 6.3). As explained in Chapter 4, the presence of two phases might be caused by some local compositional inhomogeneity (some regions should have a composition much less than 27 wt. % Mn) and the $\gamma \rightarrow \varepsilon$ martensitic transformation during furnace cooling. Fortunately, both austenitic $\gamma$ and martensitic $\varepsilon$ are antiferromagnetic which are MRI compatibility.
Fig. 6.4 and Fig. 6.5 illustrate the optical micrographs of the porous structure and the pore size distribution of the Fe-35Mn compacts with different volume fractions of NH4HCO3 addition. In addition to the porosity difference, in these compacts, the pore size was also different. It largely depends on the porogen amount. The mean and maximum pore sizes in the prepared Fe-35Mn alloys are also included in Table 6.2. As shown, the average pore size in the compacts decreased with decreasing porosity level. The pore size in the Fe-35Mn sample without NH4HCO3 was in the micrometer range (ca. 7 μm in diameter), which suggests that these micro-pores might be caused by the Kirkendall effect, alloying and liquid phase sintering [158]. When 10% of NH4HCO3 spacer was added, much larger pores with the size up to ca. 134 μm were formed; the mean pore size was ~31 μm. Those pores were deemed to be left after the decomposition of the porogen NH4HCO3. Even larger macropores (~200 to ~500 μm) were observed if the spacer amount increased to 20 vol.%. It was noted that these macropores had a size larger than the NH4HCO3 particles (20 to ~100 μm in diameter), suggesting that these macropores might result from the spacer particles assembly that later evaporated during debinding stage. In summary, the pore size and porosity largely depend on the selection of the space holding material and its characteristics. The greater amount of porogen generally results in higher porosity. The larger particle size leads to a larger pore size in the sintered compact. However, it is also...
noted in this study that the maximum amount of NH4HCO3 was 20 vol.%, beyond which the powder mixture was not compressible.

Figure 6.4 - (a) Microstructure of sintered Fe-35Mn alloys by different powder mixtures with (a) no porogen, (b) 10 vol.% NH4HCO3 and (c) 20 vol.% NH4HCO3.
6.3.3 Degradation (corrosion) behavior evaluation

6.3.3.1 Electrochemical analysis

Fig. 6.6 displays the Tafel plots of the Fe-35Mn alloys samples in 5% NaCl and SBF solutions. The corrosion potential tested in the 5% NaCl solution was -0.68 to -0.86V, as compared to -1.0V for pure Fe in 3.5% NaCl solution [144]. When tested in the SBF solution, the current density was approximately -0.8V, which was comparable with that of Fe-35Mn measured in the Hank’s solution (-0.74V reported in Ref. [3]).

Table 6.3 summarizes the degradation current density of each sintered sample. As can be seen, porous Fe-35Mn samples sintered from NH₄HCO₃-containing compacts showed a faster electrochemical degradation, as compared to the samples without NH₄HCO₃ addition. This was expected because the addition of NH₄HCO₃ induced more porosity, particularly open-cell porosity, which effectively increased exposure areas in the corrosive
solutions. The degradation rate approached 5.61 and 8.28 mmpy in the 5% NaCl solution for the 10 vol.% and 20 vol.% NH₄HCO₃ samples. In the SBF solution the degradation rates were 3.72 and 5.26 mmpy respectively. Noteworthy was the degradation results in SBF, which were about six times higher than that of the cold rolled Fe-35Mn alloys (i.e., 0.7 mmpy reported in [15]), and 20-fold higher than that of cast-wrought Fe (0.16 mmpy in [54]) in the modified Hank’s solution. In the 5% NaCl solution, the samples degraded much faster than in SBF (Table 6.3). It was clear that the degradation was largely dependent on the porosity in the Fe-Mn alloys, which could be adjusted by the amount of porogen addition.

Table 6.3 - Degradation rate in 5% NaCl and SBF solutions calculated from Tafel plots.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Material</th>
<th>$I_{corr}$ (µA cm⁻²)</th>
<th>CR (mmpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 % NaCl</td>
<td>No porogen</td>
<td>170 ± 13</td>
<td>2.34 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>10 vol.% porogen</td>
<td>322 ± 59</td>
<td>5.61 ± 1.02</td>
</tr>
<tr>
<td></td>
<td>20 vol.% porogen</td>
<td>447 ± 43</td>
<td>8.28 ± 0.80</td>
</tr>
<tr>
<td>SBF</td>
<td>No porogen</td>
<td>144 ± 21</td>
<td>1.99 ± 0.28</td>
</tr>
<tr>
<td></td>
<td>10 vol.% porogen</td>
<td>214 ± 19</td>
<td>3.72 ± 0.34</td>
</tr>
<tr>
<td></td>
<td>20 vol.% porogen</td>
<td>284 ± 34</td>
<td>5.26 ± 0.63</td>
</tr>
</tbody>
</table>

* $I_{corr}$ - corrosion current density; CR - corrosion rate; mmpy – mm per year.
Figure 6.6 - Polarization curves of porous Fe-35Mn alloys in 5% NaCl and SBF solutions.
6.3.3.2 Static immersion test

Fig. 6.7 presents the degradation rate obtained from the immersion test. The degradation of the Fe-35Mn samples gradually slowed down over immersion time. This could be related to the fact that the degradation products of Fe-35Mn were not soluble. These insoluble degradation products mostly adhered and accumulated onto the sample surface, thus slowing down the ion exchange between the substrate and solution.

Figure 6.7 - Degradation rate of porous Fe-35Mn alloys in 5 % NaCl and SBF solutions determined in static immersion tests.
Fig. 6.8 compares the SEM images of the degradation products of various samples after 3 days of immersion, in either 5% NaCl or SBF solution. A few important findings could be summarized. Firstly, the amount of degradation product depended on the porosity; the sample degraded more severely if it had a higher porosity (Figs. 6.8 (a) and (e)). Secondly, whether the corrosion products were able to adhere on the sample surface was also dependent on porosity. For instance, the corrosion products adhered firmly on the Fe-35Mn sample, while the products lost intactness to the surface of the Fe-35Mn-20 vol.% NH₄HCO₃ sample. Thirdly, the degradation was more severe in the 5% NaCl than in SBF for all the samples. These observations were in good agreement with the degradation results, shown in Table 6.3 and Fig. 6.6. After 14 days immersion, degradation became so severe that large cracks appeared and the samples started to lose their integrity. The solution became semi-transparent or opaque with orange colour insoluble substances suspending in it. Dark black pasty-like corrosion products were found on the sample surface. EDS analysis revealed that the corrosion products were composed of Fe, Mn, O, P, S and Ca for the sample soaked in the SBF. However the Fe-to-Mn weight ratio of the corrosion product was much lower than 65:35, which suggested Mn was easier to corrode in the solution.
Figure 6.8 - SEM images of the degradation products on the Fe-35Mn samples after 3 days immersion (a) Fe-35Mn, in 5% NaCl (b) Fe-35 Mn, in SBF (c) Fe-35Mn- 10 vol.% NH₄HCO₃ in 5% NaCl, (d) Fe-35Mn-10 vol.% NH₄HCO₃ in SBF, (e) Fe-35Mn- 20 vol.% NH₄HCO₃, 5% NaCl, and (f) Fe-35Mn- 20 vol.% NH₄HCO₃, SBF.
From the above observations, we propose a degradation model, which is primarily based on corrosion of iron or steel. When the Fe-Mn alloy is immersed in NaCl or SBF solutions, the anodic reaction is:

\[
\begin{align*}
Fe \rightarrow Fe^{2+} + 2e^- & \quad \text{(Eq. 6.1)} \\
Mn \rightarrow Mn^{2+} + 2e^- & \quad \text{(Eq. 6.2)}
\end{align*}
\]

Since the corrosive medium is exposed to the atmosphere, it contains dissolved oxygen. The cathodic reaction is then:

\[
O_2 + 2H_2O + 4e^- \rightarrow 4 OH^- \quad \text{(Eq. 6.3)}
\]

In the uniform corrosion, sodium and chloride ions do not partake in the reaction. The overall reaction is then:

\[
\begin{align*}
2 Fe + 2 H_2O + O_2 \rightarrow 2Fe^{2+} + 4 OH^- & \rightarrow 2Fe(OH)_2 \downarrow \\
\text{or} \quad 2 Mn + 2 H_2O + O_2 \rightarrow 2Mn^{2+} + 4 OH^- & \rightarrow 2Mn(OH)_2 \downarrow
\end{align*}
\]

(Fig. 6.4)

Ferrous hydride and manganese hydride precipitate from solution. In oxygenated solutions these hydrides are further oxidized to Fe(OH)₃:

\[
4 Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4 Fe(OH)_3 \quad \text{(Eq. 6.5)}
\]

Considering the existence of open-cell pores in the samples, another type of corrosion – crevice corrosion – also likely occurs in these pores in addition to general corrosion described above by Eqs. 6.4 and 6.5. Inside the pores, the oxygen is depleted because of the restricted convection so that the oxygen reduction (Eq. 6.3) ceases in the pores. Such oxygen depletion has a significant indirect effect with increasing exposure time. Reaction 6.1 or 6.2 tends to produce an excess of cations, which has to be balanced by the migration of Cl⁻ anions (note that OH⁻ ions may also migrate but they are less mobile than Cl⁻). As a result, metal chloride hydrolyses in water [159]:

\[
Fe^{3+}Cl_2 + 2H_2O \rightarrow Fe(OH)_2 \downarrow +2H^+Cl^- \quad \text{(Eq. 6.6)}
\]
During crevice corrosion, both chloride and hydrogen ions accelerate the dissolution rate of metals (Eq. 6.3 or 6.4). The increase in dissolution, in turn, increases migration and the result is therefore an autocatalytic process. The corrosion mechanisms in SBF are thought to be identical to that in 5% NaCl, as discussed above. Nevertheless, since the chloride concentration in SBF is much lower than in the 5% NaCl, the corrosion kinetic in SBF is slower.

6.3.3.3 Dynamic immersion test

In addition to the static immersion test (Fig. 6.8), a dynamic immersion test was also performed to mimic blood flow inside the coronary artery. Fig. 6.9 shows the corrosion rate of the Fe-35Mn alloys with 0%, 10% and 20% of NH₄HCO₃ in both 5% NaCl and SBF solutions over a period of 30 days dynamic immersion time. Several data points were collected during immersion. The conversion of the weight loss into corrosion rates revealed that, for all the three samples, the corrosion rate decreased with the immersion time extending. In 5% NaCl solution, the overall corrosion rate of the samples without NH₄HCO₃ was approximately 8 mmpy after 1 day immersion. However, for the ones with 10% and 20% NH₄HCO₃, their corrosion rates almost reached 11 and 16 mmpy. After 30 days immersion in 5% NaCl solution, the overall corrosion rates all dropped to ca. 2 mmpy for all the samples. The corrosion rates in SBF were slightly slower than those in 5% NaCl solution, which was in an agreement with the static immersion test. The slower corrosion rates in SBF revealed the weaker corrosion ability of SBF than 5% NaCl solution.

Comparing these dynamic immersion results with static immersion test, samples in this dynamic circulation system degraded much faster than those in static environment. During immersion corrosion (both static and dynamic), the accumulation of the corrosion products always occurred on the sample surfaces. In dynamic cyclic system, the flowing liquid was able to flush off some of the corrosion products and expose the fresh bare surface to the corrosive solution. Thus the flowing solution accelerated the entire corrosion process. This system mimicked the circulation of the blood in vivo. Thereby, it better illustrated the occurrence of the implant’s degradation inside human body.
Figure 6.9 - Corrosion rate calculated after dynamic immersion test (a) in 5% NaCl and (b) in SBF, as a function of immersion time.

6.3.3.4 Ion Release

Fig. 6.10 shows the evolution of the concentrations of iron and manganese ions in solutions during a one-month’s dynamic degradation test. There was little difference in ion concentrations for all the specimens up to 7 days. After that the specimens produced with porogen released more ions than that without porogen. It also could be seen that the released ion concentration of iron was slightly higher than that of manganese. This could be due to the fact that the Fe-35Mn alloy contained more Fe than Mn.
6.3.4 Mechanical properties

6.3.4.1 Tensile properties

In general, the mechanical properties of PM alloys are considerably sensitive to porosity. A lower porosity offers a higher effective load-bearing cross-sectional area, and therefore leads to a higher mechanical strength.

Fig. 6.11 displays the typical stress-strain curves for the sintered Fe-35Mn alloys with different volumes of NH\(_4\)HCO\(_3\) addition. The mechanical properties including the hardness, UTS and ductility derived from such tests are presented in Table 6.4 It was found that the
UTS of the sintered compacts was reduced from about 50 to 20 MPa and the elongation decreased from about 1.1 to 0.7%, while the Rockwell hardness value decreased from about 34 to 13HRH, if the porogen amount increased from 10 vol.% to 20 vol.%. The addition of porogen led to a decrease of mechanical properties by increasing the porosity in the test pieces.

Figure 6.11 - Tensile stress-strain curves of Fe-35Mn compacts with 0%, 10% and 20% spacer.

Table 6.4 - Mechanical properties for Fe-35Mn sintered compacts produced with different volumes of porogen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total porosity (%</th>
<th>Hardness (HRH)</th>
<th>UTS (MPa)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With 0% porogen</td>
<td>27.3 ±0.6</td>
<td>33.78±2.25</td>
<td>50.7±4.21</td>
<td>1.11±0.15</td>
</tr>
<tr>
<td>With 10 vol.% porogen</td>
<td>40.0 ± 3.9</td>
<td>27.72±2.01</td>
<td>30.1±1.57</td>
<td>0.95±0.21</td>
</tr>
<tr>
<td>With 20 vol.% porogen</td>
<td>48.2 ± 0.3</td>
<td>13.58±1.98</td>
<td>20.2±2.54</td>
<td>0.74±0.12</td>
</tr>
</tbody>
</table>
6.3.4.2 Fractography

Fig. 6.12 shows some typical microscopic fractography of the sintered Fe-35Mn alloys with different volume fractions of NH₄HCO₃ addition after tensile tests. As illustrated, all fractured pacts exhibited a typical brittle failure. It could be clearly seen that all the sintered compacts with and without the addition of porogen material exhibited some river pattern cleavage feature, a characteristic of brittle fracture. As indicated in the close-up images (Fig. 6.12 (b)), there were some small and shallow dimples (red arrows) on the fracture surface of those compacts which was the trace of the ductile fracture. But there were barely any dimples in 10% and 20% spacer samples, shown in Figs. 6.12 (d) and (f). This was caused by discrete particles. In the highly porous Fe-35Mn alloy (pores were interconnected and irregular in shape) the particle bonding was considerably weak, resulting in some particles being detached by the tension force. Therefore, the intergranular rupture dominated the fracture in the 10% and 20% porogen samples.

Overall, the SEM images of the fracture surfaces of the porous Fe-35Mn samples showed that cracks were propagated along the pores in the material. The highly porous structure with large pore size and high porosity level in the sintered compacts led to a brittle fracture mechanism. In some area where the well-consolidated portion might experience ductile deformation and thus the shallow dimples were observed. In summary the porosity level and the pore size in the sintered Fe-35Mn material had a significant effect on the tensile behavior.
Figure 6.12 - Fracture surfaces of the as-sintered Fe-35Mn alloys produced with different additional volumetric portion of NH₄HCO₃ (a) 0%, (c) 10%, (e) 20%, (b), (d) and (f), the close up image of (a), (c) and (e).
6.4 Summary

In this study, porous Fe-35Mn alloys were produced with NH₄HCO₃ as porogen (space holding). Fe-35Mn alloys with 0, 10 and 20 volumetric percent of NH₄HCO₃ were produced by a simple blend-press-sinter method in current chapter. The effect of the addition of porogen on the microstructure evolution, densification, corrosion behavior as well as mechanical properties of the sintered Fe-35Mn compacts was studied.

- The main phases presented in the sintered samples were antiferromagnetic austenitic $\gamma$ and martensitic $\varepsilon$.
- The degradation rate of the Fe-35Mn samples obtained by introduction of the NH₄HCO₃ porogen was significantly accelerated when compared with the samples without NH₄HCO₃ addition.
- Potentiodynamic analysis revealed a degradation rate ranging from ca. 2 to 8 mmpy in both 5% NaCl and SBF solutions, which met the degradation requirement with a 6 ~ 12 months service life for a biodegradable material.
- The proposed degradation mechanisms were uniform corrosion in addition to crevice corrosion.
- The mechanical properties of these porous Fe-35Mn alloys were not satisfactory. This poses a limitation for certain bioapplications.
Chapter 7 Stress Corrosion Cracking (SCC) of Fe-35wt.%Mn Alloys

7.1 Introduction

In the previous chapters, the mechanical properties and corrosion properties were presented for the Fe-35wt.%Mn alloys produced by various techniques. As with any load-bearing material, the corrosive environment (e.g. blood and intercellular fluid) with the stress could lead to stress corrosion cracking (SCC) [160, 161]. SCC is a complicated form of corrosion. An interaction amongst a susceptible material, the corrosion environment and the applied stress is involved in SCC. The crack formation and crack propagation would lead to a premature failure. Therefore SCC is a necessary consideration while designing a biodegradable implant.

Riepe et al. [162] had investigated SCC of Nitinol and found that SCC fracture could even occur on such a corrosion resistant material. The SCC susceptibility of Mg-based materials had also been studied recently [163-167]. However, the literature on SCC behavior of the Fe-35Mn alloy is very limited. One of few studies is by Hermawan et al. [161], based on an immersion test. SCC evaluation can be carried out with different techniques. Among these, slow strain rate testing (SSRT) is an accelerated laboratory testing method. SSRT, also known as constant extension rate tensile testing (CERT), is a standard method of materials testing [168, 169]. Metallic specimen is subjected to extension at a constant rate. The load is varied to maintain the constant extension rate. Although the in-service implants do not experience the same loading conditions in SSRT, this accelerated test is able to provide reliable information on the SCC susceptibility and has been used to study the SCC of many materials in the literature. For example, Humphries et al. used the SSRT method to study SCC mechanism in mild steel [170]. It has also been applied in titanium alloys by Powell et al. [171], austenitic stainless steels [172] and aluminium [173].

The SSRT results are used to evaluate the resistance of the material to environmentally assist cracking. As stated in ASTM G129 standard [168], the SCC susceptibility can be quantified using many methods, such as:
(1) Time-to-failure ratio, the ratio of time-to-failure determined for the material in the test environment \( TTF_e \) to the corresponding value determined in the control environment \( TTF_c \):

\[ \text{RTTF} = \frac{TTF_e}{TTF_c}. \quad \text{(Eq. 7.1)} \]

(2) Plastic-elongation ratio \( (RE) \), the ratio of plastic elongation determined for the material in the test environment \( E_e \), to the corresponding value determined in the control environment \( E_c \) where plastic elongation is approximated to be the difference in crosshead displacement from the onset of specimen yielding to crosshead displacement at specimen fracture:

\[ \text{RE} = \frac{E_e}{E_c}. \quad \text{(Eq. 7.2)} \]

The use of plastic elongation instead of total elongation minimises variabilities between test results from differences in test machine compliance, which are most significant in the elastic region of the load displacement curve.

(3) Reduction-in-Area ratio \( (RRA) \), the ratio of reduction in area after fracture for the specimen in the test environment \( RA_e \) to the corresponding value determined in the control environment \( RA_c \):

\[ \text{RA} = \frac{RA_e}{RA_c}. \quad \text{(Eq. 7.3)} \]

(4) Notch-tensile-strength ratio \( (RNTS) \), the ratio of the notch tensile strength determined for the material in the test environment \( NTSe \) to the corresponding value determined in the control environment \( NTSc \):

\[ \text{RNTS} = \frac{NTSe}{NTSc}. \quad \text{(Eq. 7.4)} \]

The other methods also include fracture mechanics approaches. As introduced above, although all the methods are ATSM standardized, they are not applicable for our current material. In our study, the synthesized Fe-35Mn alloy samples were not fully dense material, so that the reduction of area after SSRT would not be evident. For the same reason, the plastic elongation was not obvious either in most samples. Therefore we used
an alternative method proposed by Abe et al.[127]; the index $I_{SCC}$ was calculated as per Eq. 7.5 from the stress-strain curves.

$$I_{SCC} = \frac{1 + \varepsilon_n}{1 + \varepsilon^{SCC}} \times \frac{P_n}{P^{SCC}} - 1 \quad \text{(Eq. 7.5)}$$

where $\varepsilon_n$, $P_n$ are strain and load at maximum load in the load-elongation curves obtained in noncorrosive environments, and $\varepsilon^{SCC}$, $P^{SCC}$ are strain and load at maximum load in load-elongation curves obtained in corrosive environments. The larger the $I_{SCC}$ value, the higher the specimen’s susceptibility to SCC [127].

In this chapter, the SCC of Fe-35Mn alloy in a physiological environment was studied using the SSRT method. The mechanical properties, the SCC susceptibilities calculated from the obtained mechanical properties and the fractography were investigated. This investigation will help provide better understanding with regard to the stress corrosion behavior specifically for this alloy.

### 7.2 Experimental

Two groups of samples were used: one was produced by blended elemental (BE) powder (the same powder as in Chapter 4) and the other was fabricated by the prior mechanically milled (MMed) powder (the same powder as in Chapter 5). The two groups of samples were named as BE and MMed samples. The powders were uniaxially compacted under 400MPa and then sintered in vacuum at 1200 °C for 4 hours with a heating rate of 10 °C/min. The MMed Fe-35Mn had finer particles ranging from 18 to 33μm while the BE Fe-35Mn had bigger particle sizes ranging from 40 to 63μm. In terms of porosity, the sintered sample from the MMed Fe-35Mn powder had a porosity of ~ 10%; whereas the sintered samples from BE Fe-35Mn had a porosity of ~ 25%.

In this experiment, the test pieces were cut from the sintered compacts made from both BE and MMed powders. The geometry and dimensions of the SSRT samples and the SSRT system were described in Chapter 3 and shown again in Fig. 7.1. The exposed gauge area of the test specimen was subjected to the corrosive solutions (5% NaCl or SBF). Two different strain rates of $\times 10^{-5}$s$^{-1}$ and $\times 10^{-6}$s$^{-1}$ (corresponding to crosshead speeds of 0.02 and 0.002 mm/min) were selected to investigate the effect of strain rate on the mechanical strength. The procedure complies with the ISO standard 7359–Part 7. All the tests were
conducted at room temperature. For comparison, the SSRT tests were also performed in air (i.e. without corrosion) under the same strain rates.

Figure 7.1 - (a) The sketch of tensile testing sample (scale 4:1) and (b) the schematic of the experimental set-up of the SSRT system.

7.3 Results and discussion

7.3.1 SCC susceptibility

The SCC susceptibility is indicated by a decrease in mechanical properties of the material after SSRT [174]. The stress vs. strain plots of the Fe-35Mn specimens produced by BE powder and MMed powder at different testing strain rates in different testing solutions are presented in Figs. 7.2 and 7.3. Table 7.1 lists the calculated SCC susceptibility index of the BE and MMed Fe-35Mn alloys under different testing conditions. The relationship between $I_{SCC}$ and testing strain rate derived from Table 7.1 is illustrated as bar diagrams in Fig. 7.4. Generally, in both SBF and 5% NaCl corrosive media, the mechanical properties
of all the specimens were significantly reduced for each strain rate. The detailed analysis is further explained below.

7.3.1.1 Effect of corrosive environment on SCC susceptibility

From Figs. 7.2 and 7.3, it could be seen that both BE and MMed Fe-35Mn alloys failed at a much lower stress and strain in the corrosive media than in air. Moreover, the loss was more severe when both BE and MMed samples were tested in 5% NaCl, as they fractured at a lower ultimate tensile strength (UTS) and strain than in SBF solution. Take the BE samples tested at a strain rate of $10^{-6}$ for example (Fig. 7.2 (b)), UTS and elongation values in air were about 72 MPa and 1.0% while the values in 5% NaCl and SBF were around 56 MPa, 0.65% and 61 MPa, 0.85%, respectively. This trend was also observed for MMed Fe-35Mn alloy and for other testing strain rates.

The SCC susceptibility $I_{SCC}$ presented in Table 7.1 and the comparison charts Fig. 7.4 also represented the trend stated above that the $I_{SCC}$ of BE samples tested at $10^{-6}$ strain rate were 1.16 in 5% NaCl and 0.60 in SBF. The results indicated that the loss of the mechanical properties at failure was indeed a result of the synergistic effect of stress and corrosive environment.

The occurrence of a higher $I_{SCC}$ in 5% NaCl than in SBF was ascribed to the higher ion concentration of Cl$^-$ in 5% NaCl. The presence of Cl$^-$ ion is the main cause of corrosion in Fe-based biodegradable metals [63]. The protective hydroxide layer formed from the cathodic reaction will be destructed by those chloride ions. These SCC susceptibility results showed an agreement with the report by Sedriks [175]. The SCC susceptibility of 304 stainless steel in chloride-rich corrosive media at 100 °C showed an increased $I_{SCC}$ which was also related to the increased Cl$^-$ ion concentration.
Figure 7.2 - Typical stress vs strain curves obtained from SSRT of Fe-35Mn produced of BE powder at strain rate (a) $10^{-5}\text{s}^{-1}$ and (b) $10^{-6}\text{s}^{-1}$. 
Figure 7.3 - Typical stress vs strain curves obtained from SSRT of Fe-35Mn produced of MMed powder at strain rate (a) $10^{-5}\text{s}^{-1}$ and (b) $10^{-6}\text{s}^{-1}$.

7.3.1.2 Effect of strain rates on SCC susceptibility

The results in Fig. 7.3 showed that the MMed tensile specimens tested in SBF at a nominal strain rate of $10^{-5}\text{s}^{-1}$ fractured after reaching a maximum stress level of about 193 MPa with a strain at fracture value of 1.91%. In contrast, the MMed tensile specimens in the
Chapter 7 Stress Corrosion Cracking of Fe-35wt.%Mn Alloys

same environment failed at around 181MPa showing a strain at fracture of about 1.78% when $10^{-6} \text{s}^{-1}$ was applied.

As shown in Table 7.1 and Fig. 7.4, the $\text{I}_{\text{SCC}}$ of MMed tensile specimens tested in SBF at a nominal strain rate of $10^{-5} \text{s}^{-1}$ was around 0.24, ~50% lower than that obtained at the strain rate $10^{-6} \text{s}^{-1}$ (i.e. 0.49). It can be inferred that in both corrosive environments, both type of alloys were considerably sensitive to the changes in strain rate. Similar results were reported by Tjong [176], who confirmed the SCC susceptibility of austenitic Fe-Al-Mn specimens was highly dependent on the applied strain rate [177]. A slower testing strain rate led to a longer exposure period of specimen into the corrosive solution. This subsequently enabled more chloride ions to attack the surface, created more initiation sites and produced deeper holes and pits - all contributed to the crack initiation and propagation, leading to a more rapid failure at $10^{-6} \text{s}^{-1}$ strain rate than at $10^{-5} \text{s}^{-1}$.

7.3.1.3 Effect of porosity on SCC susceptibility

As listed in Table 7.1 and shown in Fig. 7.4, at both strain rates, in both corrosive media, BE Fe-35Mn alloys showed a considerably higher $\text{I}_{\text{SCC}}$ than the MMed alloys, in agreement with the lower fracture UTS and apparent strain for the BE samples presented in Figs. 7.2 and 7.3. The $\text{I}_{\text{SCC}}$ of MMed Fe-35Mn alloys tested in 5% NaCl solution at a strain rate of $10^{-6}$ was about 0.85 while the value for the BE sample was approximate 1.16. The SCC susceptibility of the BE Fe-35Mn in 5% NaCl was 1.5 times higher than the MMed sample at the same condition.

In all environments and strain rates studied, the SCC susceptibility of the BE Fe-35Mn was more dominated than the MMed Fe-35Mn specimens. In other words, the BE Fe-35Mn samples were more sensitive to the changes in environment and change of strain rate, in comparison to the MMed samples. This was mainly due to the difference in the porosity level between these two groups of samples as illustrated in Fig. 7.5. The BE samples had a porosity level ranging from ca. 22% to 27% while the MMed samples had a porosity of approximate 8% to 12%. The much higher porosity in the BE samples resulted in a much lower UTS and a higher SCC susceptibility in the testing conditions.
Table 7.1 - SCC susceptibility indices of Fe-35Mn alloys produced by BE powder and MMed powder in different testing environments at various strain rates.

<table>
<thead>
<tr>
<th>Starting powder</th>
<th>Testing environment</th>
<th>Iscc $10^{-5}$</th>
<th>Iscc $10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE</td>
<td>5% NaCl</td>
<td>0.85±0.17</td>
<td>1.16±0.18</td>
</tr>
<tr>
<td></td>
<td>SBF</td>
<td>0.38±0.07</td>
<td>0.60±0.12</td>
</tr>
<tr>
<td>MMed</td>
<td>5% NaCl</td>
<td>0.66±0.15</td>
<td>0.85±0.10</td>
</tr>
<tr>
<td></td>
<td>SBF</td>
<td>0.24±0.03</td>
<td>0.49±0.08</td>
</tr>
</tbody>
</table>

Figure 7.4 - Relationship between Iscc and strain rates of Fe-35Mn produced by (a) BE powder and (b) MMed powder.
7.3.2 Fractography after SSRT

7.3.2.1 Effect of test environment

Fig. 7.6 represents a typical fracture surface of the BE and MMed Fe-35Mn specimen tested in air at a constant strain rate of $10^{-6}$ s$^{-1}$. The overall fraction of fracture surface of both BE and MMed samples suggests the intergranular (or precisely inter-particle) brittle failure occurring due to the weak particle bonding. The occasional instances of the dimples, shown in (b) and (d), also appeared in some areas.
Figure 7.6 - Typical fractograph of the Fe-35Mn alloys tested at a constant strain rate of $10^{-6}$ in air: (a) fracture surfaces of BE and (c) MMed Fe-35Mn alloys; (b) and (d) the fracture surface at higher magnification of (a) and (c).

Figs. 7.7 and 7.8 displays the fractographs of the BE and MMed specimens tested in both SBF and 5% NaCl solutions at the strain rate of $10^{-6}$s$^{-1}$. The overall fracture mechanism of both samples is brittle fracture. There were hardly any dimples found on either BE or MMed specimens failed in both corrosive solutions. As indicated by red circles and arrows, intergranular cracks appeared in the samples tested in both SBF and 5% NaCl solutions. Compared to the samples tested in 5% NaCl, the samples tested in SBF demonstrated a less number of intergranular cracks. The phenomenon of the appearance of intergranular cracks was caused by particle detachment; however the corrosion occurring during SSRT test amplified the occurrence of the crack forming [178]. By comparing with the fracture images in air (shown in Fig. 7.6), it was evident that the corrosive environments
significantly affected the fracture morphology and the types of corrosive solution dominated the SCC susceptibility of Fe-35Mn alloys. The 5% NaCl solution led to a much higher SCC susceptibility than SBF.

By comparing between the BE and MMed specimens (shown in Figs. 7.7 and 7.8), the appearance of the intergranular cracks in the BE samples was wider than in the MMed specimens. This might be caused by the different geometry of the pores in the BE samples – the pores in these samples were mainly interconnected. More surface areas were exposed to the corrosive solution because of the presence of pores.

Figure 7.7 - Fractographs of the BE Fe-35Mn specimen tested at the strain rate of $10^{-6}$ s$^{-1}$: (a) in SBF, (c) in 5% NaCl solution and (b), (d) the evidence of intergranular cracking (indicated by arrow) of (a) and (c) respectively.
7.3.2.2 Effect of strain rate on the fracture surface

Fig. 7.9 presents the fractographs of the BE and MMed specimens tested in 5% NaCl solution at different strain rates. The intergranular branching were more visible on the fracture surface of both BE and MMed samples at a slower strain rate of $10^{-6}\text{s}^{-1}$. Comparing between Figs. 7.9 (a) and (b), the cracks (red arrows) propagated deep within the pores of the BE Fe-35Mn specimen when tested at $10^{-6}\text{s}^{-1}$. The size and length of cracks revealed the more severe effect of SCC. This was also observed in the MMed Fe-35Mn specimens in which more and deeper cracks were found on the surface (red arrows) when the specimen was tested at a slower strain rate. This further affirmed that both BE and MMed specimens had a higher SCC susceptibility at a slower strain rate. During SCC, if the strain rate was slow, the interaction between corrosive solution and
A corrodlible specimen was accelerated, in particular, in the inter-particle boundaries, around the pores and/or at the grain boundaries [166].

Figure 7.9 - Fractographs of the BE and MMed specimens tested in 5% NaCl solution at different strain rates (a) BE sample at $10^{-5}$ s$^{-1}$, (b) BE sample at $10^{-6}$ s$^{-1}$, (c) MMed sample at $10^{-5}$ s$^{-1}$ and (d) MMed sample at $10^{-6}$ s$^{-1}$

From the above observations of SCC fracture, in both corrosive media (SBF and 5% NaCl solution), an overall brittle failure with intergranular cracking happened in the SCC region while the SCC was manifested by the presence of intergranular cracking (in red circles and pointed out by red arrows in Figs. 7.7, 7.8 and 7.9) [178]. Generally, SCC of austenitic alloys in rich chlorides condition is usually in the form of intergranular cracking [160, 161]. There were no ductile dimples appeared in SCC area while a mixed mode (ductile and brittle) fracture happens in an inert environment (air).
The intergranular cracking was further confirmed in the macroscopic images, as shown in Fig. 7.10. The SCC affected zone was characteristic of the intergranular cracking and the appearance of iron oxides was verified by EDX analysis. It was noted that even in a ductile austenitic alloy the intergranular cracking could take place, because the selective dissolution at the crack tip might effectively lower the fracture toughness $K_{lc}$ and result in dissolution-controlled cleavage [161, 179].

Figure 7.10 - Fractographs of the overall fracture surface of BE Fe-35Mn alloy tested in 5% NaCl at $10^{-6}$s$^{-1}$. 
7.4 Summary

The SSRT in physiological environments had been performed on the BE and MMed Fe-35Mn alloys in order to assess their SCC susceptibility $I_{SCC}$ through mechanical properties. The fractography after the SSRT were also observed. A few conclusions were listed below:

- Both the BE and MMed Fe-35Mn alloys in 5% NaCl failed at lower mechanical properties than in SBF, indicating 5% NaCl solution is more corrosive and hence the Fe-35Mn alloys had a higher SCC index.
- Both specimens failed at lower mechanical properties when SSRT were performed at a lower strain rate. The slower strain rate led to a higher SCC susceptibility.
- The BE Fe-35Mn was more sensitive in corrosive medium than the MMed samples, indicating that BE alloys were more susceptible to SCC in a physiological environment.
- Intergranular fracture was observed on the sample surface of all tested specimens.
- Cracks were larger and deeper in more corrosive 5% NaCl and at slower strain rate at $10^{-6}$s$^{-1}$.
- SCC initiated from crevices and pores in both BE and MMed Fe-35Mn alloy.
Chapter 8 Cytocompatibility of Fe-35wt.%Mn Alloys

8.1 Introduction

As a potential biomaterial for implant applications, the developed Fe-35wt.%Mn alloy must be evaluated in terms of its biocompatibility. One essential requirement for Fe-35Mn to be used in living tissues is its ability to avoid any adverse effect. The Fe-35Mn is biodegradable and during its biodegradation, ion (Fe and Mn ions) release to the surrounding tissues is a critical issue that needs to be carefully examined.

Ideally the material to be used needs to be evaluated both in vitro and in vivo. Usually the in vitro cell culture studies are the first step of the biocompatibility evaluation. [180]. In an early study, the cell compatibility of Fe-35Mn powders directly contacting with 3T3 mouse fibroblast cell line was investigated [13]. However, little is known about the influence of iron and manganese ions on the cells.

In our preliminary study, we attempted to culture L929 cells directly onto Fe-35Mn bulk metal. However the resazurin agent (used for fluorescence reading) showed a reaction with Fe-35Mn specimen. This would influence the following data reading or even cell growth. Therefore, in this study we used an indirect contact method, also commonly known as elution testing, to evaluate the in vitro local cytocompatibility of the released iron and manganese ions on cells.
8.2 Experimental

In order to investigate the cytocompatibility of Fe-35Mn alloys with an indirect method, the elution of Fe-35Mn alloys should be firstly prepared. Following the preparation of the elution, different amounts of Fe-35Mn extractions were added to culture wells to make up a 1ml medium for cell growth. Murine fibroblast cell line L929 was selected for mammalian cell culture experiments. Cell proliferation was measured using a resazurin fluorescence assay, which was used to quantify viable cells at various stages of proliferation. The detailed experimental procedure had been introduced in Chapter 3.

Measurement of fluorescence value is a simple and commonly used method for cell proliferation. Typically, the fluorescence reading curves of the cell proliferation are generated as a function of time and compared with statistical methods. Occasionally the curves overlap with each other, making it difficult to distinguish the cell growth. Here, we propose an alternative method of quantitatively assessing cell proliferation curves, by calculating the area under the curve (AUC). Fig. 8.1 displays a typical example for using the AUC method to assess tumor growth curves. The AUC is, mathematically, an integral of the curve with respect to culturing time. The AUC represents the total cell growth over time. With this method, the cell proliferation can be quantitatively evaluated and the cell proliferation behavior can be straightforwardly compared, using the AUC values between different test groups.

In this experiment, the AUC values were obtained using the GraphPad Prism software (La Jolla, CA). AUC was calculated by selecting “XY analysis” and then “Area under curve” functions from the “analyze” tool. The “select” button was used to select the appropriate curves. A screenshot of the GraphPad Prism software is shown in Fig. 8.2.
Figure 8.1 - Use of AUC method for tumor growth analysis: (A), Representative growth curves form six groups; (B), Plotting area under the curve (AUC) for three typical curve: 1 (rapidly growing), 2 (growing and regressing), and 3 (no growth) [181].

Figure 8.2 - A screenshot of the GraphPad Prism software.
8.3 Results and discussion

8.3.1 Ion release of testing solution

The released iron and manganese ion concentrations of the Fe-35Mn alloys elution were 6.44 and 5.69 ppm respectively, after immersion of the sample in sterilized SBF solution for 24 hours at 37 °C. To prepare different testing extraction concentrations, different volumes of 2, 10, 20, 100 and 200μl were added into separate wells in order to make up a 1ml testing medium. The final Fe and Mn ion concentrations of each well were then calculated and listed in Table 8.1. The highest iron and manganese ion concentrations were 1.29 and 1.12 ppm respectively. Medium control and blank were also prepared for the following fluorescence reading.

Table 8.1 - Fe and Mn ion concentrations in each well.

<table>
<thead>
<tr>
<th>Specimen ID</th>
<th>Ion concentration (ppm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Mn</td>
</tr>
<tr>
<td>Initial extraction</td>
<td>6.44</td>
<td>5.69</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>10</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>20</td>
<td>0.13</td>
<td>0.11</td>
</tr>
<tr>
<td>100</td>
<td>0.64</td>
<td>0.57</td>
</tr>
<tr>
<td>200</td>
<td>1.29</td>
<td>1.12</td>
</tr>
<tr>
<td>SBF control</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Medium control</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Blank</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>
8.3.2 Cell proliferation

Fig. 8.3 shows the typical weekly results of resazurin fluorescence assay using L929 cells before growing in Fe-35Mn extracts and after cell culture for another 3 individual days. The growth of L929 cells in various extraction volumes ((2, 10, 20, 100 and 200μl) and in SBF and medium controls was measured daily over this four-day period. The Day 1 data presents the initial reading of cells after the first day’s incubating in medium (allowing cells attach onto the plate bottom). The Day 2, 3 and 4 data reveal to the readings of cells after being cultured in Fe-35Mn extractions for up to 3 days. As shown, curves obtained from each concentration including the controls entangled together. It could hardly be predicated that there was any difference on the cell proliferation. Hence the AUC method was selected to represent the cell growth.

![Figure 8.3 - Indirect cytocompatibility of L929 cells after cultured in different extraction volumes (2, 10, 20, 100 and 200μl) of the Fe-35Mn alloy and the controls of SBF and cell-culture medium over a 4 day period. RFU: Relative fluorescence units](image)

Figure 8.3 - Indirect cytocompatibility of L929 cells after cultured in different extraction volumes (2, 10, 20, 100 and 200μl) of the Fe-35Mn alloy and the controls of SBF and cell-culture medium over a 4 day period. RFU: Relative fluorescence units
Figure 8.4 - AUC plots for (a) 2\,\mu\text{l}, (b) 10\,\mu\text{l}, (c) 20\,\mu\text{l}, (d) 100\,\mu\text{l}, (e) 200\,\mu\text{l}, (f) SBF control, (g) medium control and (h) summary of all AUC
In order to clarify the use of AUC, the individual AUCs of all seven curves in Fig. 8.3 are plotted in Fig. 8.4. The AUC value for each of these curves was determined as described in Methods (Section 8.2.1). Figs. 8.4 (a) to (e) represent the AUCs of cell growth in Fe and Mn ions environment with different extraction volumes from 2 to 200μl per well. Figs. 8.4 (f) and (g) represent the AUCs of SBF and medium controls. Fig. 8.4 (h) illustrates an overall comparison of all the AUCs from Figs. 8.4 (a) to (g).

The AUCs of all the cell growth curves over all three weeks’ testing were then determined using the GraphPad Prism tools. These data were expressed as L929 cell growth and were related to the medium control, which was considered to correspond to 100% viable cells. These specific values displayed in Fig. 8.5 showed that all testing groups with various Fe and Mn ion concentrations and SBF control maintained the cell viability at about 100% during the whole incubation period. The minor differences between testing wells with controls were not conclusively evident to prove the influence of SBF and metal ions on the growth of L929 cells. Therefore, it was compatible for L929 cells to grow in an environment containing up to 1.29 and 1.12 ppm iron and manganese ions.

Figure 8.5 - L929 mammalian cell proliferation in Fe-35Mn alloy SBF extraction with SBF and cell-culture medium as controls.
8.3.3 Morphology of L929 cell

Fig. 8.6 shows the L929 cell morphologies after the first day’s culture with no Fe-35Mn alloy extractions in the tissue culture plate. The first day’s culture allowed the cells being able to adhere on the bottom of each well. After seeded on the bottom, cells would be ready for the following cytocompatibility test (cultured in medium with extractions). There were no differences in Fig. 8.6 images that the same amount of cells were added in each well. Most of the cells in each well were of oval shape, implying that cells start to stick to the bottom while the free cells have round morphologies.

Optical morphologies of cells after four-day exposure to different concentrations of extraction are depicted in Fig. 8.7. Cells cultured in the SBF and medium control images are also presented. Comparing with the images before adding any extractions shown in Fig.8.6, the cell number increased to a certain extent during the 4-day culture period for all groups. There was no obvious difference between control groups and experimental groups. This result corresponded to the cell proliferation data. Most cells appear elongated in a spindle shape and become aligned at some parts with high cell densities. Fig. 8.8 illustrates a close-up image of the cells after 4 day incubation in the ion concentration of 200μl per well. The marked A, B and C indicated the cell morphologies at different stages; they were initially attached (A), firmly attached (B) and during cell division (C), respectively.

Consequently, there was no apparent influence on the number of cells after the 4 days incubation in the range of 0 to 1.29 and 0 to 1.12ppm of released iron and manganese ion concentrations. Cells had grown healthily during this incubation period. In other words, it was considered safe and biocompatible for cells to live in these concentration levels.
Figure 8.6 - Optical microscopic images of L929 mammalian cells after the first day’s incubation in different wells (a) 2µl, (b) 10µl, (c) 20µl, (d) 100µl, (e) 200µl, (f) SBF control, (g) medium control.
Figure 8.7 - Optical microscopic images of L929 mammalian cells after the 4 days incubation at different ion concentrations (a) 2μl, (b) 10μl, (c) 20μl, (d) 100μl, (e) 200μl, (f) SBF control, (g) medium control.
8.4 Summary

*In vitro* cytocompatibility tests were performed to evaluate the potential of Fe-35Mn alloys as biodegradable implant materials. Indirect cell tests using Murine fibroblast cell line L929 were carried out using SBF extractions from the alloys and the results indicated acceptable cytocompatibility.

- The results of resazurin fluorescence assay showed that the testing environment with different ion concentrations did not have significant influence on cell growth. Cells proliferate normally in a medium containing up to 1.29 and 1.12ppm Fe and Mn ions respectively.
- The microscopic images of cells before and after incubation in Fe and Mn ions containing environment also presented a slight proliferation during the culture period. Thus, the material is considerably biocompatible since no significant difference was found in cell viability response to the materials’ elutes, when compared with the controls.
Chapter 9 Conclusions and Future Work

This chapter summarizes the main findings from the previous chapters and makes some recommendations for future work.

9.1 Conclusions

In this thesis, the Fe-35wt.%Mn alloys were powder metallurgically (PM) fabricated by three different starting powders: blended elemental (BE) Fe-Mn powder, mechanical milled (MMed) Fe-Mn powder and BE Fe-Mn powder with NH₄HCO₃ as porogen. The microstructures evolution, densification, corrosion behavior as well as mechanical properties of the sintered Fe-35Mn compacts were evaluated. The stress corrosion cracking (SCC) behavior and biocompatibility of produced Fe-35Mn alloys were also investigated. The following conclusions can be summarized.

PM Fe-35Mn alloys were firstly prepared by a simple blend-press-sinter method, with varying sintering temperatures and holding times. The porosity level of the sintered Fe-Mn compacts was controlled by the sintering parameters. By increasing the sintering temperature and holding time, the porosity level of the sintered compacts decreased. This was closely related to the powder densification – a diffusion controlled process. Potentiodynamic analysis revealed a degradation rate ranging from ca. 1.5 to 4 mmpy in both 5% NaCl and SBF solutions, which met the degradation requirement with a 6 ~ 12 months service life for a biodegradable material. However, the mechanical properties were insufficient, which were closely related to the porosity and lower level of densification.

A series of mechanical milling (MMing) conditions were carried out, including milling time and ball-to-powder (B-P) ratio to fabricate denser Fe-35Mn alloys. With increasing the B-P ratio and milling time, the particle size decreased and partial diffusion of Mn into Fe particles occurred. A B-P ratio of 5:1 and a milling time of 6 hours were proofed to be the most suitable milling condition to MM the Fe-Mn powder. After MMing, various die compacting pressures were applied to compact Fe-35Mn powder, followed by cold isostatic pressing (CIPing) at 200MPa. A higher compaction pressure led to a lower porosity level and CIPing further enhanced the samples’ densification after sintering. The MMing process significantly densified powder compacts by reducing the starting powder size. When compared with BE Fe-35Mn alloys, the sintered Fe-35Mn samples from
MMed powder demonstrated a lower degradation rate but higher than fully solid Fe-35Mn alloys reported in the literature. All samples, with porosity being from 6.5% to 12.2%, revealed a degradation rate from 0.6 to 1.4 mm/year. Better mechanical properties were also achieved with the UTS ranging from 190 to 240 MPa.

Porous Fe-35Mn alloy foam samples were fabricated through the use of ammonium bicarbonate (NH₄HCO₃) particles as porogen (space holder). 0, 10 and 20 volumetric percent of NH₄HCO₃ were added into Fe-Mn powder mixture and then a simple blend-press-sinter method was then employed. After the addition of the porogen, interconnected pores were formed and porosity level was then greatly enhanced. As a result, the use of space holding technique was an effective approach to accelerate the corrosion rate. The corrosion rates obtained from potentiodynamic analysis reached ca. 2 to 8 mmpy in both 5% NaCl and SBF solutions. Nevertheless, poor mechanical properties of these porous Fe-35Mn alloys posed a limitation for load-bearing applications.

The main phases presented in all the sintered Fe-35Mn samples (BE, MMed and porous) were austenitic γ and martensitic ε, which could be beneficial to the magnetic resonance imaging (MRI) compatibility due to their anti-ferromagnetic property. The porosity level dominated the corrosion rates and mechanical properties. The proposed degradation mechanisms by immersion tests were uniform corrosion in addition to crevice corrosion. The fracture mechanism of Fe-35Mn compacts sintered under different conditions showed a dominant brittle fracture while only a few dimples were observed in the MMed samples.

The SCC susceptibility of BE and MMed Fe-35Mn alloys was assessed by a slow strain rate test (SSRT) method in physiological environments. The SCC susceptibility increased with slowing the testing strain rate and also varied with the corrosive media. BE samples with more crevices and pores were more sensitive to SCC compared with MMed samples. Intergranular fracture was observed to be dominant in the occurrence of SCC. SCC started from crevices and pores in both BE and MMed Fe-35Mn alloys.

The biocompatibility of Fe-35Mn alloys was evaluated via an indirect contact method that murine fibroblast cell line L929 was selected to be cultured in SBF extractions from the alloys. Cells proliferated normally in a medium containing up to 1.29 and 1.12ppm Fe and Mn ions and the cells exhibited healthy growth in the Fe and Mn ion rich medium.
9.2 Future work

The following work is recommended for future investigations in order to produce more suitable Fe-35Mn alloys as bioscaffolding materials and to gain better understandings of the biocompatibility.

(i) Optimize the production method to increase mechanical properties while maintaining satisfactory degradation rate.

(ii) Dynamic immersion test of Fe-35Mn in simulated body fluid (SBF) needs to be carried out for even longer time and at 37°C to simulate the in vivo corrosion environment in the human system. The ion release of Fe and Mn ions also needs to be conducted under this condition.

(iii) Conducting further in vitro degradation study to understand the formation and dissolution of degradation layer.

(iv) Other cell lines should be tested, in order to confirm the cell compatibility of Fe-35Mn alloys. The cell lines include MC3T3 mouse calvaria osteoblast cell line and CRL-11372 human fetal osteoblast cell line.

(v) In vitro blood compatibility of Fe-35Mn alloys needs to be studied, since the developed materials have the potential application in intravascular stenting. The blood compatibility test includes haemolysis assay and platelet adhesion assay.
References


168. *Standard practice for slow strain rate testing to evaluate the susceptibility of metallic materials to environmentally assisted cracking,* in *Standard ASTM G129-00.* 2006, ASTM International West Conshohocken, PA.


