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Development of Ternary Fe-Mn-Si Biodegradable Alloys
Via
Powder Metallurgy

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Abstract

Recent years have seen extensive investigations on Fe-based alloys proposed as degradable biomaterials for temporary biomedical implants. Among all the Fe-based degradable biomaterials (DBMs), Fe-Mn-Si alloys are considered as promising candidates due to their excellent mechanical properties, good biocompatibility and degradability in a physiological environment. All the investigated Fe-based DBMs including Fe-Mn-Si alloys, however, present a limitation of low degradation rate. This inhibits the further application of Fe-Mn-Si alloys as DBMs. Powder metallurgy (PM) may provide a practical way to overcome the low degradation rate of the currently developed Fe-Mn-Si DBMs. This is because PM as a near-net-shape technique presents the ability to synthesis porous products with controlled porosities. The porous structures in the PM Fe-Mn-Si alloys enable to provide more areas for degradation, and thereby improving the degradation rate. So far, Fe-Mn-Si alloys are traditionally fabricated by the cast/wrought route, and little work has been discussed in terms of the powder sintering behaviours of Fe-Mn-Si alloys. This is another motivation to explore the sintering behaviour of Fe-Mn-Si alloys. In this research, mechanical milling (MM) was employed to produce Fe-Mn-Si powder mixtures with homogeneous dispersion and fine microstructure, while the traditional press-and-sinter route was applied to densify the Fe-Mn-Si compacts.

A series of Fe-28Mn-xSi alloys (wt.%; x = 0, 1, 2, 3, 4) produced via the PM route were compared in terms of degradation rate, densification and mechanical properties in order to identify the optimal Si content in the ternary Fe-Mn-Si DBMs. It was found that the degradation rate, densification and mechanical properties largely depended on the Si content in the sintered Fe-Mn-Si compacts. The degradation rate of the sintered Fe-Mn-Si alloys decreased with the increase of Si content. The density of the sintered Fe-Mn-Si alloys increased significantly with increasing Si content. With an increase in Si content, the tensile strength dramatically increased while modulus of elasticity increased only mildly. Based on the above results, the PM Fe-28Mn-3Si alloy is thought to be a good candidate for DBMs.

Both MM and blended element (BE) Fe-28Mn-3Si powder mixtures were pressed and sintered at four different sintering temperatures (i.e., 1000, 1100, 1200 and 1300°C) for 3h.
The density of the MM alloys increased drastically with the increase of sintering temperature. By contrast, no densification occurred in the BE alloys at all sintering temperatures. The phase constituents of the sintered BE alloys varied with the sintering temperatures. Predominant $\gamma$-austenite and minor $\varepsilon$-martensite were observed in the BE alloys sintered at temperatures $\leq 1200$ °C. However, $\text{Mn}_3\text{Si}$ intermetallic phase was identified in the BE alloy sintered at 1000 °C. Interestingly, only a single $\alpha$-Fe phase is detected in the BE compacts when the sintering temperature increased to 1300°C. The MM alloys are comprised of duplex phases at all sintering temperatures: main $\gamma$-austenite along with $\varepsilon$-martensite. The pore size of MM alloys decreased significantly with increasing sintering temperature, while high sintering temperatures ($\geq 1200$°C) led to the formation of large pores (~150µm in size) in BE alloys. The mechanical properties of MM alloys, were remarkably higher than their BE counterparts. Mn depletion region (MDR) was identified on the surface of both the BE and MM alloys. The thickness of the MDR layer increased with the increase of sintering temperature. The Mn concentration increased parabolically with the increase of the distance from the surface (x=0) of the sintered alloys until stabilizing at ~ 27wt.%. The thickness of MDR layer in the sintered BE compacts was significantly larger than their MM counterparts. The sublimation of Mn in the sintered alloys was largely responsible for the weight loss of all the sintered compacts. The weight loss of all the sintered alloys increased significantly with the increase of sintering temperature. The weight loss of the MM alloys was much lower than their BE counterparts.

Fe-28Mn-3Si alloys sintered at 1200°C for various isothermal time (i.e., 0, 1h, 2h, 3h) were fabricated. The isothermal time dependence of densification, mechanical properties and Mn sublimation was studied. It was found that the densification and weight loss of the sintered Fe-Mn-Si alloys mainly occurred at the first hour of isothermal holding. The MDR region increased with the increase of isothermal time. It was also revealed that a long isothermal time (>1h) has little influence in the mechanical properties.

The mechanical properties of the sintered Fe-28Mn-based samples as a function of immersion time in SBF solutions were evaluated. In addition, a preliminary biocompatibility test was performed for the sintered alloys. A severe deterioration in mechanical properties has been found in both Fe-Mn and Fe-Mn-Si alloys after being soaked for ≥ 45 days. The cell viability
test demonstrated that both Si-free and Si-containing alloys had no inhibition on the proliferation of L929 cells.
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### Chapter 5

Chapter 5 is extracted from the published journal paper of 'Effects of mechanical milling and sintering temperature on the densification, microstructure and tensile properties of Fe-Mn-Si powder compacts'. Journal of Materials Science & Technology, http://dx.doi.org/10.1016/j.jmst.2016.08.024

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**CO-AUTHORS**

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<td>Peng Cao</td>
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**Certification by Co-Authors**

The undersigned hereby certify that:

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- that the candidate wrote all or the majority of the text.

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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 7 is extracted from the published journal paper of 'A comparative study of powder metallurgical (PM) and wrought Fe–Mn–Si alloys'. Materials Science and Engineering: A, 630, 116-124.

| Nature of contribution by PhD candidate | Experimental design, experimental operation, paper writing and further polishing |
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Chapter 1 Introduction

1.1 Background

Metallic biomaterials are widely employed to repair or replace the diseased or damaged tissue in body fluid due to their superior mechanical properties, excellent corrosion resistance and good wear resistance, as well as reasonable biocompatibility [1-4]. Currently, popular metallic biomaterials available in the market include stainless steels, Ti-based and Co-Cr-based alloys [5-7]. They have become essential biomaterials for load-bearing implants such as artificial hip joints and bone fixation devices [8, 9]. It is interesting that all the clinically used metallic biomaterials present a common characteristic of high corrosion resistance. This means that implants with high corrosion resistance would stay permanently in the human body unless an additional surgical operation is undertaken. However, in some cases such as blockage of cardiovascular vessels and bone fracture, permanent implantation is unnecessary after the restoration of the diseased or damage tissue [10, 11]. This is because permanent implantation can lead to various complications such as physical irritations, chronic inflammation, thrombosis and in-stent restenosis [12, 13]. Taking blockage of cardiovascular vessels for instance, placing stents as a scaffold to open the narrowed vein is an effective and economic treatment. Clinical studies have shown that the remodelling and healing process of blocked vessels could last an average period of 6~12 months (See Figure 1.1) [14-16]. After the remodelling of the blocked artery, the presence of stents would be redundant or even harmful to the already healed tissues. However, currently available stents are made of biomaterials with high corrosion resistance. This inevitably results in many complications mentioned above. To deal with the complications, patients have to take anti-platelet drugs such as aspirin and ticlopidine for the long term [17-19]. Alternatively and perhaps more effectively, they have to receive a second surgery to remove the implanted stents, which is expensive and may damage the healed vessels [20, 21].
Figure 1.1  Relationship between the mechanical integrity and degradation of a biodegradable stent (Note: The purple, red and blue curves in this figure represent that the degradation rates of the biodegradable stents are too slow, moderate and too fast, respectively) [14-16].

Fe-based degradable biomaterials (DBMs) are a good option for implants only requiring temporary intervention. The degradability, as a unique advantage of DBMs in comparison to corrosion-resistant biomaterials, enables to address problems caused by permanent implants. Iron is an indispensable trace element in the human body as it is involved in a variety of essential metabolic processes such as oxygen sensing and transport, catalysis, DNA synthesis and electron transport[22]. It is estimated that a healthy adult man and woman contains approximately 55 and 45 mg·kg⁻¹ of iron, respectively [22, 23]. The majority of body iron (around 60%~70%) is incorporated into haemoglobin in circulating red blood cells. Another 20-30% of body iron is stored as ferritins and hemosiderins in hepatocytes and reticuloendothelial macrophages [23-29]. Iron deficiency can give rise to a series of adverse effects, including iron-deficiency anemia or chronic inflammation[30].

Fe-based DBMs are mainly proposed as temporary implants including stents and bone fixation devices (pins, nails and plates). It is recommended that stents should disappear entirely in 24 months after the remodelling of narrowed arteries [31]. As for broken bones,
ideally, broken bones could be recovered over a period of 12 to 18 weeks [32]. This implies that bone fixation devices should break down after a time scale of 12 to 18 weeks. However, the degradation rate of the currently investigated Fe-based DBMs is too low, to match the required degradation rate. This seriously impedes Fe-based DBMs to be used as DBMs.

1.2 Motivations for this study

In this project, Mn and Si were selected as alloying elements in Fe-based DBMs. Mn and Si are trace elements in the human body. The summary of the pathophysiology of Mn and Si can be viewed in Table 1.1 [33-35].

<table>
<thead>
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<th>Element</th>
<th>Pathophysiology</th>
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<tr>
<td>Manganese</td>
<td>Essential trace element                                                                                                    Normal blood serum level: 1μm/L   Important role in metabolic cycle of lipids, amino acids and carbohydrates Activator of enzyme Influences the function of the immune system, bone growth, blood clotting, cellular energy regulation and neurotransmitter synthesis Scavenger of free radicals in the manganese superoxide dismutase</td>
</tr>
<tr>
<td>Silicon</td>
<td>Essential mineral                                                                                                              Distributes in tissues such as bone, nails, tendons, walls of the aorta and red blood serum Normal blood serum level ≈ 20–44mg/kg Important role in aiding the healing process and helping to build the immune system Important for the growth and development of bone and connective tissue</td>
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In addition, it is believed that the addition of Mn in Fe matrix can increase the degradation susceptibility of Fe-Mn-based alloys [36]. Eqs. (1.1) and (1.2) [37] show that the standard electrode potential of Mn is much lower than that of Fe. In this case, the degradation potential of Fe-Mn-based alloys is supposed to be decreased if a Fe-Mn-based solid solution is formed [36].

\[
Fe \rightarrow Fe^{2+} + 2e^- \quad E = -0.44V \quad (1.1)
\]

\[
Mn \rightarrow Mn^{2+} + 2e^- \quad E = -1.18V \quad (1.2)
\]

However, the main motivation for selecting Mn and Si stems from a reported investigation into the degradation and cytotoxicity of a cast Fe-30wt.%Mn-6 wt.%Si alloy [38]. It was
reported that the Fe-30Mn-6Si alloy presented a higher degradation rate in comparison with pure Fe and the binary Fe-30wt.%Mn. Moreover, it is also shown that the Fe-30Mn-6Si exhibited a reasonably good biocompatibility. All reported results suggested that Fe-Mn-Si alloys could be promising candidates for DBMs.

Powder metallurgy (PM) technique can be a solution to further improve the degradation rate of currently investigated Fe-Mn-Si alloys. This is because PM, as a near-net-shape technique, can produce Fe-based alloys with tailored porosities. The pores in the PM Fe-Mn-Si alloys can provide more degradation area, which is beneficial to accelerating the degradation process of the PM Fe-Mn-Si alloys. In this project, mechanical milling (MM), powder blending (BE) and vacuum sintering were employed to investigate the consolidation of Fe-Mn-Si alloys.

It is noted that a Mn concentration of 28 wt.% was selected in this project. This was determined by the following consideration:

Ternary Fe-Mn-Si alloys exhibit good shape memory effect (SME), although the investigation of SME was beyond the scope of this project. It is believed that SME of the Fe-Mn-Si is governed by stress induced ε-martensite, while the pre-existing thermal induced ε-martensite suppresses the formation of stress induced ε-martensite and leads to the degradation of SME [39, 40]. Figure 1.2 reveals that the thermal induced ε-martensitic phase decreases with the increase of Mn concentration, and disappears completely when Mn content is more than 27 wt.%. Thus, a Mn concentration of 28 wt.% was chosen.
1.3 Research objectives

The aim of this project is to study the feasibility of PM route to synthesise Fe-Mn-Si DBMs. The specific objectives are grouped into three different aspects and summarised as below.

(1) Development of Fe-Mn-Si DBMs with an optimal Si concentration.

Si, as an alloying element in PM Fe-Mn-Si DBMs, may affect the densification, mechanical properties and the degradation rate of PM Fe-Mn-Si alloys. However, it is pointed out that there has been little work to illustrate the relationship between the Si concentration and degradation rate of the ternary PM Fe-Mn-Si alloys in a physiological environment. Therefore, it is my aim to investigate how Si concentration changes the degradation rate of PM Fe-Mn-Si alloys. Accordingly, casting/wrought Fe-Mn-Si alloys with same compositions were fabricated and analysed for comparison purposes. In addition, the effect of Si on the densification and mechanical properties of the PM Fe-Mn-Si alloys was investigated as well.
(2) Investigation of the effect of sintering parameters on the microstructure and mechanical properties of the PM Fe-Mn-Si alloy at an optimal composition.

Sintering parameters including sintering temperature and sintering time play key roles in the microstructure and mechanical properties of ternary PM Fe-Mn-Si alloys. This project focuses on studying the influence of sintering temperature and sintering time on microstructure and mechanical properties’ evolution of PM Fe-Mn-Si alloys.

(3) Study of sublimation of Mn in PM Fe-Mn-Si alloys under high vacuum environment during sintering.

The sublimation of Mn in PM Fe-Mn-Si alloys is an issue that should be investigated due to the high vapour pressure of Mn. The sublimation of Mn may change the final composition of the produced PM Fe-Mn-Si alloys. In this project, sintering temperature and sintering time dependence of Mn sublimation in Fe-Mn-Si alloys were analysed and discussed during vacuum sintering.

(4) Assessment of the biocompatibility of the sintered Fe-Mn-Si alloys.

The index of biocompatibility determines whether the sintered Fe-M-Si alloys can be used as DBMs. In this section, preliminary evaluation on the biocompatibility of the sintered Fe-Mn-Si alloys was carried out.

1.4 Thesis outline

This thesis is comprised of 9 chapters, and part of the chapters are based on the published or submitted papers by the author of this thesis. Chapter 1 briefly overviews the project. Chapter 2 reviews the applications of the powder metallurgy on Fe-based alloys, as well as a latest progressive in mechanical properties, degradation behaviour and biocompatibility of Fe-based degradable biomaterials (DBMs). Chapter 3 illustrates the experimental setup and procedures. Chapter 4 discusses the sublimation behaviour of Mn in Fe-28wt.%Mn-based alloys during vacuum sintering at various sintering temperatures between 1000°C and 1200°C.
Chapter 5 illustrates the effects of sintering temperature and mechanical milling on the densification, microstructure and mechanical properties of Fe-28wt.%Mn-3wt.%Si compacts. Chapter 6 presents the effect of isothermal time on the microstructure and mechanical properties of the sintered mechanical milling (MM) Fe-28wt.%-3wt.%Si alloy. Chapter 7 compares the mechanical properties, microstructure and degradation performance of the sintered Fe-28wt.%Mn-xSi alloys to their wrought counterparts. Chapter 8 studies the mechanical properties of the Fe-28wt.%Mn-3wt.%Si alloys immersed for various durations in SBF solution and the biocompatibility of the sintered Fe-28wt.%Mn-3wt.%Si samples. Chapter 9 summarises the key findings and provides some suggestions for future research.
Chapter 2 Literature review

2.1 Introduction

Iron (Fe) is the fourth most abundant element in the earth’s crust [42]. Fe and its alloys are versatile metals which are widely used in the civil engineering, aerospace, medical and automotive domains [43-46]. It is noted that medical/surgical applications have become a fast growing segment of Fe and its alloys. Stainless steels, as an important part of Fe family, for example, are gold standard biomaterials for permanent implants such as artificial hips, knees, cardiovascular stents and dental structures [3, 47, 48]. In recent years, research revealed that permanent implants made of corrosion-resistant biomaterials such as Ti alloys and stainless steels are unnecessary in applications such as temporary bone fixation devices (pins, plates and nails) and stents [49-51]. This is because long term implantation of these permanent implants can cause various chronic complications, and even a second surgical operation to remove implants. By contrast, degradable biomaterials enable avoidance of a second surgical operation due to their degradability in the human body. In this case, degradable biomaterials are considered ideal materials to replace the permanent implants for such temporary applications.

More recently, it was found that some specific types of Fe-based alloys can be potential candidates for degradable biomaterials due to their outstanding mechanical properties, reasonable degradability and good biocompatibility [52]. The conception of using Fe-based alloys as degradable/corrodible biomaterials was raised by Peuster et al [53], which can be traced back to a decade ago. The investigation demonstrated that pure iron presented the feasibility of becoming degradable biomaterials for the first time.

This chapter first presents a general introduction relevant to the science of powder metallurgy. In addition, an extensive literature review in relation to a latest progressive in mechanical properties, degradation behaviour and biocompatibility of Fe-based degradable biomaterials (DBMs) is illustrated.
2.2 Brief introduction to powder metallurgy

Powder metallurgy (PM) is an extensively employed technique to synthesise and process ferrous alloys [54-56]. The PM technique presents a variety of well-proven advantages in comparison with casting. As a near-net shape technique, the PM technique, for example, allows manufacture of ferrous products with precise tolerances [57-59]. This enables avoidance, or greatly reduces the subsequent finishing process, which is significantly beneficial to reduce the waste of materials and thereby decreasing the cost of industrial production. In addition to that, PM technique is a simple and competitive way to control the microstructure of the fabricated materials [60, 61]. This is favoured to produce PM parts with a tailored function. For instance, the superior PM technique has been widely used to synthesis cellular materials with customized porosity and pore size for specific applications such as biomedical materials [62], bearings and filters [63-65]. In general, a typical PM route consists of four main steps, including powder mixing, shaping, and sintering [66].

2.2.1 Mechanical milling

Powder mixing is a common yet still essential procedure in the PM industry. Powder mixing, as the name implies, is a treatment that obtains powder mixtures (powders involving two or more types of metallic powder) with uniform distribution. In past decades, a variety of useful powder mixing devices have been developed for powder blending such as the turbula, static mixer and V-shaped drum [67]. Among all the powder mixing techniques, mechanical milling (MM) is an effective and inexpensive approach to gain homogenised and fine powder mixture. Figure 2.1 shows the schematic diagram of the ball and powder rotation in a vial during MM [68, 69]. Mechanical milling, also known as ball milling, is a technique to blend and grind powders with uniform distribution in a mill along with a rational proportion of balls [70]. In contrast to the conventional mixing technique performed by the turbula and V-shaped drum, a significant advantage of the MM technique is that MM can effectively reduce the particle size of the powder mixtures due to the repeated welding and fracturing of the powder particles in a ball mill [69]. The refined particle size can significantly reduce diffusion distances between powders, which contributes to enhancing the densification in the following sintering process. Further, the plastic deformation of the powders caused by the mechanical collision of grinding medium (e.g. steel balls and cemented carbide balls) may introduce a
large amount of crystal defects such as dislocations, vacancies and extra external surfaces as well as grain boundaries [69, 71]. The unstable imperfections with a high state of energy contribute to the solidification of the MM powder mixture in the following sintering step.

Figure 2.1 The schematic diagram of the ball and powder motion in the vial during mechanical milling [68, 69].

MM is a complex process. The important MM parameters for obtaining the desired powder mixtures includes milling vial, grinding medium, rotation speed, milling time, weight ratio of ball-to-powder, milling atmosphere and process control agent [69, 72].

The materials used for producing the milling vial and grinding medium play an essential role in the final properties of the milling powder mixture. If the components of the materials used for the milling vial and grinding medium are different from that of the powder, the powder can be contaminated due to the materials being dislodged from the vial and grinding medium. Therefore, materials with good wear resistance are usually selected to minimize the contamination of the powder. The materials most frequently used for the vial and grinding medium are hardened steel, stainless steel and WC-Co [73-75].

A proper rotation speed should be selected. It is well-known that the energy input to the powder increases with the increase of rotation speed [76, 77]. This implies that a faster
rotation speed of the grinding balls gives rise to a higher driving force to reduce the powder size. However, a critical (maximum) rotation speed exists during milling [78, 79]. The milling balls would pin on the inner wall of the milling vial due to a large centrifugal force if the rotation speed is larger than the critical speed [69]. This would eventually decrease the collision probability between the powder and the milling balls, and consequently decreases the efficiency of the ball milling process. Therefore, it is important to choose a reasonable rotation speed.

Milling time is one of the most important variables in the MM process. The grain size, in general, decreases with the increase of milling time [80, 81]. However, excessive milling time may lead to the agglomeration of particles due to the high surface energy of fine particles. Moreover, the milling time required to obtain the desired microstructure is closely related to the weight ratio of ball-to-powder, milling atmosphere and process control agent.

The weight ratio of ball-to-powder significantly affects the ball milling efficiency. In general, an increase of the weight ratio of ball-to-powder promotes the ball milling efficiency. This is because a high weight ratio of ball-to-powder increases the probabilities of collision between milling balls and powder particles [69]. In other words, a higher weight ratio of ball-to-powder accelerates the refinement process of the powder particles. Consequently, a high weight ratio of ball-to-powder decreases the milling time required.

Milling atmosphere is usually used to prevent the powder particles from oxidation during milling process. The most commonly employed atmosphere is an inert gas such as argon or helium.

Process control agents, sometimes referred to as organic surfactants, are of great importance to avoid the agglomeration of particles, as well as refining the particle size of powders in MM process[82-84]. The most popular process control agents in industry and scientific research are steric acid, ethyl acetate, polyethylene glycol and ethanol [66, 85]. During milling, the process control agents enable adsorbance on the surface of the powder particles, thereby impeding a direct clean powder-to-powder contact. Consequently, the small amount of surface additive minimises the agglomeration and cold welding of powder particles, and promotes the fracturing milling process. However, the quantity of the additives in powder
mixtures must be controlled. In general, the amount of the process control agent added to powder mixtures is less than 3% (in weight percent) [69]. The main reason for this is that the decomposition of the organic additives in the following de-waxing and sintering process releases a larger amount of carbon and oxygen. This may react with the metal powders and thereby lead to the formation of harmful carbides and oxides [86].

Over the years, a number of attempts have been made to produce Fe-Mn-Si powder mixtures with a single γ-austenite phase using MM technique.

Saito et al [87] studied the effect of the MM technique on the phase transformation of the elemental Fe-30Mn-6Si (in weight percent) powder mixture as a function of ball milling time. They reported that α-ferrite phase partially transformed into γ-austenite phase after 5h ball milling (See details in Figure 2.2). Interestingly, a single γ-austenite phase was detected when the MM duration was ≥ 20h. A similar research performed by Liu et al. [88] implied that Fe-24Mn-6Si powder presented a single metastable γ-austenite phase after MM, which is in good agreement with the results from Saito.

![Figure 2.2 XRD results of Fe-30Mn-6Si powder mixture milling for various durations [87].](image)

Figure 2.2 XRD results of Fe-30Mn-6Si powder mixture milling for various durations [87].
2.2.2 Powder shaping

Powder shaping is an essential part of the conventional PM process. Die compaction and metal injection moulding are two commonly employed powder shaping techniques in PM industry and research.

Die compaction is a long-established, cost-efficient and easy-to-practise powder shaping technique. As the name suggests, die compaction is a process of pressing loose powder to green compacts through upper and lower punches under applied uniaxial external pressure at certain temperature. The main steps involving in the die compaction are powder filling, compaction and ejection, as shown in Figure 2.3 [66]. During die compaction, pressure is the most important parameter that must be considered as the density of the green compacts is largely determined by the pressure [89]. The external pressure applied typically ranges from 100 MPa to 1200 MPa, depending on a number of factors such as the particle size, the hardness of the particles and die-wall friction. However, it is noted that the die compaction technique cannot produce green parts with intricate geometries in the orientation perpendicular to the pressing direction due to the ejection of the green compacts from the die cavity.

![Figure 2.3 Typical die compaction setup][66].
Metal injection moulding (MIM) technique is an intelligent near-net shaping technique, which originated from plastic injection moulding and conventional PM technology. MIM is capable of shaping metallic powders with complex geometries that is not possible via die compaction. It has been utilized to fabricate a broad range of products in medical/dental, aerospace and automotive applications [90]. In general, the MIM process consists of the following steps [91]: (1) Creating a homogeneous mixture of the selected metal powders and a suitable binder. Typically, the binder is a thermoplastic polymer comprising several inorganic substances. (2) Feedstock preparation. In this stage, the metal powders-binder mixture is granulated into pellets, which is also known as feedstock. (3) Injection moulding. Melt pellets are injected into the mould cavity in order to obtain green parts with designed geometry. (4) Debinding. In this step, the binder is removed from the green compacts via solvent debinding and the subsequent thermal debinding. (5) Densification. Green parts after debinding are sintered in a furnace under high vacuum or protective gas such as Ar/He.

2.2.3 Sintering

Sintering is a bonding and densification process of green powder compacts at high temperatures. It plays a key role in determining the mechanical and physical properties of PM products such as density, strength and ductility. With the development of modern science and technology, a large number of sintering techniques have been employed to produce a variety of commercially useful and scientifically interesting materials. In recent years, novel sintering techniques such as vacuum sintering [92, 93], spark plasma sintering [94] and microwave sintering [95], have been extensively employed to densify the metal powders.

2.2.3.1 Vacuum sintering

Oxygen is a critical factor to determine the microstructure and mechanical properties of PM materials. Ellingham diagrams, first constructed by Harold Ellingham in 1944, describe the temperature dependence of the affinity of pure metals for oxygen [96]. In the PM industry, most of the metallic materials such as ferrous alloys, titanium and tungsten alloys, are sintered at high temperatures (>1100°C) due to their high melting points. Combined with the Ellingham diagrams, the PM metallic powders are extremely active to oxygen at high sintering temperatures [97]. It is common that a high concentration of oxygen in PM alloys leads to worse microstructural and mechanical properties of sintered PM products. Moreover, powders exposed to atmosphere with high oxygen concentration are liable to oxidise. The
oxides in the PM parts formed during sintering can be crack initiation sites, therefore degrading fatigue strength, corrosion resistance and ductility. Thus, it is highly necessary to control the oxygen level as low as possible. Sintering at vacuum is a desired approach to keep the oxygen concentration at low level due to the extremely low pressure ($<10^{-3}$ Pa) in the vacuum chamber during sintering.

2.2.3.2 SPS sintering

SPS sintering (Spark Plasma Sintering) is a novel vacuum consolidation technique for metallic powders under a uniaxial pressure combined with a high pulsed DC current [98]. A unique advantage of SPS sintering is that powder compacts can achieve high densification in short sintering duration (typically a few minutes) due to high ramp rates (up to 100 °C/min) [99]. This enables inhibition of the grain growth of PM Fe-based alloys, thereby promoting mechanical properties. Published reports reveal that the rapid densification of PM alloys is achieved by the combined effects of spark discharge, joule heating and electrical field effect due to a high DC pulse current [100].

Zhang et al. [101] fabricated nanocrystalline Fe-0.8%C alloys by SPS sintering from mechanically milled Fe-C powder mixture. A relative density of ~99% was achieved after SPS sintering at 600°C for 10 min. Results revealed that the sintering temperature and sintering time of SPS sintered Fe-C alloys were reduced by 200 °C and 15 min, respectively, compared to that sintered via conventional hot pressing technique. Consequently, the grain size of SPS sintered Fe-C alloys decreased by ~ 40% with respect to their hot pressing counterparts.

Saito et al. [87] produced Fe-Mn-Si shape memory alloys sintered at 900°C for 10 min via SPS sintering. The density, grain size and yield strength of the sintered Fe-Mn-Si alloys was approximately 7.2 g.cm$^{-3}$, 3 μm, and 500 MPa, respectively. Moreover, the results revealed that the mechanical properties and shape memory effect of SPS Fe-Mn-Si alloys was comparable to those fabricated by conventional casting/wrought.
2.2.3.3 Microwave sintering

Over the years, microwave sintering has been extensively investigated to fabricate various PM metals such as refractory alloys and steels [102-104]. Microwave sintering provides many benefits such as reduced sintering time, faster heating rates, low cost production, finer microstructures and improved mechanical properties [95, 105-107].

Panda et al. [108, 109] compared microwave sintering with conventional sintering (Fig. 2.4) in terms of densification of austenitic (316L) and ferritic (434L) stainless steel. It is interesting that sintering time required in the microwave furnace was 10 min. This was reduced by 90 % with respect to a conventional MoSi₂ heated horizontal tubular furnace. Moreover, the PM stainless steel produced by microwave sintering presented significantly higher density and smaller grain size. It was also suggested that the pores in the PM steel samples sintered by the microwave furnace were much smaller as against those in conventional furnace.

![Figure 2.4 Optical micrographs of sintered (a)316L and (b)434L stainless steel in conventional (left) and microwave (right) furnace[109].](image-url)
2.3 The evaporation/sublimation of Mn in Fe-based alloys

Mn is a common alloying element in steels or Fe-based alloys. Mn, for example, is an essential composition in Fe-Mn-Si-based shape memory alloys (SMAs) [110]. Fe-Mn-Si-based SMAs is a group of smart metallic materials that can revert to their original shape after heating or unloading. The revertible phenomenon of SMAs is also known as shape memory effect (SME), which is controlled by a revisable phase transformation between the $\gamma$-austenite (fcc) phase and the stress induced $\varepsilon$-marteniste (hcp) phase [111-113]. In general, appropriate Mn content can effectively reduce the stacking fault energy, strengthen the austenite as well as increase the Néel temperature ($T_N$) in Fe-Mn-Si-based SMAs [114]. More recently, Fe-Mn-based alloys have become competitive degradable biomaterials for temporary implantable biomedical devices such as bone fixation devices and cardiovascular stents [20].

The temperature for fabrication of Mn-contained steel or Fe-based alloys could normally be $>1100^\circ C$ [115-117], depending on the fabrication route. In this case, it is necessary to note that Mn evaporation/sublimation is a serious issue which must be considered during the fabrication of such alloys at high temperatures. This is because massive evaporation/sublimation of Mn may change the final composition of the proposed alloys, and consequently affect the chemical and physical properties of the fabricated products. Research conducted on 1g of pure Mn particles at normal atmospheric pressure revealed that pure Mn particles completely sublimated in a few seconds when sintering temperatures $\geq 1000^\circ C$ (More details on the sublimation time of pure Mn particles are shown in Table 2.1) [118]. Currently, pre-alloyed ferro-manganese master alloys are the most frequently used raw materials to prevent the sublimation of Mn during fabrication of Mn steels or Fe-based alloys. However, the investigation on the sublimation/evaporation of elemental Mn in Mn steels or Fe-based alloys is very scarce. Moreover, most of the available references on the evaporation/sublimation of Mn focuses on alloys with low Mn content ($\leq 5$ wt. %) [118-120]. In other words, Mn evaporation/sublimation behaviour in steels/ Fe-based alloys with high Mn content ($\geq 5$ wt.% is still uncertain.
Table 2.1 Sublimation time of 1g Mn particles (10, 20, 50μm in size) as a function of temperature [118].

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1150</th>
<th>1200</th>
<th>1250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sublimation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10μm</td>
<td>30.3</td>
<td>4.1</td>
<td>0.9</td>
<td>0.6</td>
<td>0.15</td>
<td>0.1</td>
</tr>
<tr>
<td>20μm</td>
<td>66.7</td>
<td>8.2</td>
<td>1.8</td>
<td>1.5</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>50μm</td>
<td>$1.7 \cdot 10^2$</td>
<td>20.4</td>
<td>4.5</td>
<td>3.5</td>
<td>0.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

2.4 Fe-based alloys as degradable biomaterials

The utilization of materials for medical applications can be traced back to prehistoric civilization, in which crude dental implants made of sea shells and wood were recorded [121]. However, most of the attempts by the ancients to augment the loss of physiologic function with crude materials failed due to the lack of the knowledge relating to sterilization and toxicology. The clinical practice of biomaterials as implants in the human body was not implemented until the establishment of an aseptic surgical technique by Dr J Lister in the 1860s [122]. Since then, biomaterials for artificial implants have attracted increasing attention from material researchers, chemists and biologists, along with physicians due to their essential role in improving human life [123, 124].

Over the past few decades, various metallic biomaterials (e.g. stainless steels, Co-based and Ti-based alloys) have been commercially available for orthopaedic and orthodontic applications. Metallic implants such as bone fixation devices (e.g. plates, screws and nails), artificial tooth roots and vascular stents are routinely used to recover or replace patients’ diseased or damaged tissue such as bones, teeth, blood vessels or even organs. It is noted that all commercially used metallic biomaterials including stainless steels, Co-based and Ti-based alloys are corrosion-resistant in the human body. However, in certain cases such as bone fracture and vascular occlusion, the implantation of medical devices is only temporary [125, 126]. In other words, corrosion-resistant implants must be removed from the human body by a second surgery after the tissue heals completely. An additional surgical operation significantly increases the costs and may even damage the healed tissue or organ.
Recently, degradable metallic biomaterials, typically Mg-based and Fe-based alloys, have been extensively investigated in order to avoid a second surgical procedure caused by the corrosion-resistant metallic biomaterials. Fe-based alloys, for example, have been considered as potential candidates to replace available metallic biomaterials for temporary implantation applications due to their biodegradability, good mechanical properties and proper biocompatibility in the human body [20, 127]. Currently, Fe-based alloys however, exhibited a relatively low degradation rate in physiological media [128]. The main target for researchers is to increase the degradation rate of the Fe-based alloys, and tailor the degradation rate to the requirement of the application in vivo.

2.4.1 Definition of biomaterials

Biomaterials can be defined as any material, man-made or natural in origin, used to produce biomedical devices, which treats, replaces or assists the diseased tissue or organ of the living body [123, 129]. In this case, the common feature of biomaterials is that they are inserted in the human body and are continuously or intermittently exposed to body fluids. Thus, proposed biomaterials should meet several common requirements before clinical applications.

First and foremost, an ideal biomaterial must be biocompatible in the host physiological environment. Ratner defined biocompatibility as “the ability of a material to perform with an appropriate host response in a specific application” [130]. Biocompatibility is a unique feature of biomaterials over any other materials. Biomaterials that exhibit low biocompatibility could cause many abnormal host responses such as long-term inflammation, infection, cytotoxicity, allergy problems and detrimental immunological response as long as they are implanted in the human body [131-133]. To ensure a mutually acceptable coexistence of biomaterials and tissues in the human body, a systemic biocompatibility trial both in vitro and in vivo should be carried out for the synthetic biomaterials before their final application. In general, biocompatibility tests are performed mainly by assessment of cytotoxicity, mutagenesis and/or carcinogenesis, and cell function[134].

In addition, biomaterials should achieve feasible physical and mechanical properties such as appropriate tensile strength, wear resistance, toughness and similar modulus to the bones to serve as an augmentation or replacement for the diseased or even damaged tissue[135].
load-bearing orthopaedic applications for example, orthopaedic implants such as screws and plates should keep satisfactory tensile strength and toughness to avoid losing mechanical integrity in the period of the new bone formation and healing [136, 137].

2.4.2 The classification of biomaterials

Following continuous advances in biology, medical engineering, and materials science over the past century, a broad range of sophisticated biomaterials have been successfully fabricated and commercially applied. It is necessary to classify the existed/intended biomaterials in order to clarify the application and function of different kinds of biomaterials in the medical industry.

Currently, there are different classifications for biomaterials. Based on the chemical makeup and atomic structure of materials, biomaterials can be grouped into four basic classes: metals, polymers, ceramics and biomedical composites [138]. Figure 2.5 describes briefly the evolution and history of metals, polymers and ceramics applied as biomaterials [139]. Metallic materials are the first successfully practical biomaterials in clinic, in which the typical representatives are stainless steel and cobalt-chromium alloys. Then, the first biomedical polymeric material, polymethylmethacry (PMMA) designed as denture base, was developed in the later 1940s [140]. Currently, polymeric biomaterials are extensively considered and developed as biodegradable implants for temporary medical applications such as sutures as well as drug delivery vehicles [141, 142]. In the 1960s, ceramics were also successfully introduced to biomedical family [143]. Biomedical ceramics have been used as restorative materials in dentistry and bone reconstructive materials. In terms of their biological interactions with surrounding tissues, biomaterials can be roughly divided into three categories, which are bio-inert, bioactive and biodegradable materials [144-147]. Based on applications, biomaterials can be divided into materials used in hard tissue repair and replacement, materials for soft tissue repair and replacement and materials for drug delivery, etc.
2.4.3 Potential applications of Fe-based degradable biomaterials

For decades, research has been devoted to design biomaterials with high corrosion resistance because corrosion resistance is considered as one of the most critical design criteria for the longevity and biocompatibility of biomaterials in an aggressive physiological environment. High corrosion resistance can prevent body fluid from corroding implants. This not only keeps the mechanical properties of implanted devices stable in the human body over implantation duration, but also remarkably reduces the release of non-compatible ions from the implants into the human body.

In modern society, both coronary artery disease (CAD) and bone fracture are quite common. It is reported that CAD is one of the leading causes of death in the world with approximately 7.2 million deaths each year [148]. Figure 2.6 shows the schematic of a typical blocked artery [149]. Plaque is a sticky substance comprised of fat, cholesterol, calcium and other fibrous materials [150]. Plaque can deposit and accumulate on the inner wall of the artery and lead to the blockage of coronary vessels. The accumulation of plaque gradually narrows the artery and prevents blood from flowing to the heart. Finally, this may induce heart attack when the blood flow is not enough to the heart. Implanting stents is an effective way to open and remodel the blocked coronary artery. Up till the present moment, the available stents placed
in blocked coronary arteries are permanent metallic stents with a high corrosion resistance including stainless steel (See Figure 2.7), cobalt-chromium (Co-Cr) alloys and titanium alloys [139, 151]. As for devices for fixing and recovering bone fracture like nails, screws, plates and pins (See Figure 2.8), a vast majority of them are also made of biomaterials with high corrosion resistance [151-153].

Figure 2.6  Schematic diagram of blocked artery [149].

Figure 2.7  Stainless steel stent [151].
However, in those specific areas mentioned above, medical devices are expected to be temporarily implanted [154, 155]. Permanent or long-term implants are redundant after the recovery of diseased tissue, and the continuous implantation leads to a range of harmful complications such as permanent physical irritations, long-term chronic inflammation, thrombosis, long-term endothelial dysfunction, delayed re-endothelialization, and even neointimal hyperplasia which is responsible for in-stent restenosis [12, 13]. In this case, patients have to receive long-term antiplatelet therapy or even a second surgical procedure for removal of implants, which increases costs to a large extent or may even damage the already healed tissue.

Degradable biomaterials may be an ideal solution for biomedical devices only requiring temporary presence. In the past decade, the study of degradable biomaterials has become one of the most significant trends at the forefront biomaterials [156-159]. It is predicted that many of the high corrosion-resistant /passive implants used for temporary therapeutic applications are expected to be replaced by biodegradable devices that could disappear entirely after the complete recovery of diseased /damaged tissue in the near future [142].
Degradable biomaterials can be defined as materials used for medical implants that break down completely after the healing/recovery of diseased tissue in complex physiologic environments [160]. Polymers are the first investigated degradable biomaterials [161]. Clinically, they are now widely used as suture materials which obviate a second operation to remove sutures after wound healing [162]. Biodegradable polymers, however, exhibit a limitation of relatively low mechanical properties. This seriously impedes their further applications as temporary load-bearing devices like stents, bone plates, bone screws and bone pins. Compared to biodegradable polymers, iron (Fe) not only exhibits adequate mechanical strength and fracture toughness, but also can break down in the human body under a controlled degradation rate. Hence, Fe and its alloys are preferred to be served as load bearing degradable biomaterials.

2.5 Mechanical properties of Fe-based degradable biomaterials

Mechanical properties, including tensile strength, Young’s modulus and elongation, are important indexes to degradable biomaterials development. In general, degradable biomaterials should provide adequate mechanical support to diseased tissue during the healing period. Currently, two classes of materials have been proposed for degradable biomaterials: (1) polymers such as Poly Lactic Acid (PLA) and Pteroylglutamic acid (PGA)[142], and metals including Mg-based and Fe-based alloys [163, 164]. Table 2.2 [165, 166] summarises the mechanical properties of some typical investigated degradable biomaterials (SS 316L is presented in this table as a reference). According to Table 2.2, polymeric degradable biomaterials show weak mechanical properties compared to their metallic counterparts. The low mechanical properties of polymeric degradable biomaterials impede their applications as temporary cardiovascular stents or bone fixation devices. On the other hand, metallic degradable biomaterials obviously have superior mechanical properties compared to their polymeric counterparts. Hence, metallic biomaterials including Mg-based and Fe-based alloys attracted more attentions in terms of mechanical properties. Researchers suggest that degradable biomaterials for those applications should exhibit mechanical properties approaching to SS 316L (A gold standard biomaterial for permanent implants) [166]. It is noted that Fe-based alloys are more competitive than Mg-based alloys in terms of mechanical properties, as shown in Table 2.2.
Table 2.2  Mechanical properties of typical materials proposed as biomaterials[165, 166].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Yield Strength (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L stainless steels</td>
<td>200-300</td>
<td>450-650</td>
<td>40</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>760-880</td>
<td>830-1025</td>
<td>12</td>
</tr>
<tr>
<td>Pure Fe</td>
<td>150</td>
<td>200</td>
<td>40</td>
</tr>
<tr>
<td>Electroformed Fe</td>
<td>270</td>
<td>290</td>
<td>18</td>
</tr>
<tr>
<td>Fe-35Mn alloys</td>
<td>230</td>
<td>430</td>
<td>30</td>
</tr>
<tr>
<td>Fe-10Mn-1Pd</td>
<td>850</td>
<td>1450</td>
<td>11</td>
</tr>
<tr>
<td>Pure Magnesium</td>
<td>20</td>
<td>86</td>
<td>13</td>
</tr>
<tr>
<td>AZ91D</td>
<td>150</td>
<td>230</td>
<td>3</td>
</tr>
<tr>
<td>AZ31</td>
<td>125</td>
<td>235</td>
<td>7</td>
</tr>
<tr>
<td>Mg-Zn-Mn</td>
<td>246</td>
<td>280</td>
<td>21</td>
</tr>
<tr>
<td>Mg-1Ca</td>
<td>135</td>
<td>239</td>
<td>10</td>
</tr>
<tr>
<td>Magnesium alloy</td>
<td>140–200</td>
<td>220–280</td>
<td>2–20</td>
</tr>
<tr>
<td>PGA</td>
<td>-</td>
<td>75–142</td>
<td>15–20</td>
</tr>
<tr>
<td>PLLA</td>
<td>-</td>
<td>40–140</td>
<td>5–10</td>
</tr>
<tr>
<td>DL-PLA</td>
<td>-</td>
<td>29–35</td>
<td>-</td>
</tr>
</tbody>
</table>

2.6 Degradation behaviour of Fe-based degradable biomaterials

As a kind of biomaterials used for temporary implants in the human body, a basic requirement for degradable biomaterials is that they should enable to break down with a suitable degradation rate as long as the damaged tissue or organ is recovered. More importantly, all degradable biomaterials, which are established as potential materials for temporary implant applications, should investigate and assess their biosafety/biocompatibility both in vitro and in vivo before they are clinically applied. In general, degradation behaviour evaluation of degradable biomaterials must involve the following items:
1) Degradation rate.

An appropriate degradation rate is highly essential for those degradable biomaterials implanted in the human body. This is because either a too fast or too slow degradation rate can be adverse to the patient. If the degradation rate is too fast, the degradable implants would be failure before the damaged tissue is completely healed. In other words, devices with a high degradation rate are unable to provide enough mechanical integrity to support the recovery of tissues. On the other hand, if degradable biomaterials present a too slow degradation rate, the implants would remain in the human body for a long time after complete recovery of diseased tissue. This would cause physical irritation and inflammation which may finally need a repeated surgery to remove those devices.

Currently, there are a broad range of routes which are available to evaluate the degradation rate. The typical methods include immersion testing by measuring the mass loss and electrochemical approaches such as potentiodynamic polarization, open circuit potential evolution as well as electrochemical impedance spectroscopy [167-169]. All these tests are usually performed in various body similar fluids reflecting the ion composition and pH value of human blood, such as simulated body fluid (SBF), artificial plasma, Hank’s balanced salt solution or Ringer’s solution. Details on the constituents of these solutions are listed in Table 2.3 [170-173], Table 2.4 [174-176] and Table 2.5 [177] respectively.

**Table 2.3** Ion concentration of human body plasma and simulated body fluid [170-173].

<table>
<thead>
<tr>
<th>Ion</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>HPO₄²⁻</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human body plasma</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>103.0</td>
<td>1.0</td>
<td>27.0</td>
<td>0.5</td>
</tr>
<tr>
<td>SBF</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>147.8</td>
<td>1.0</td>
<td>4.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Table 2.4 Chemical composition of Hank’s solution [174-176].

<table>
<thead>
<tr>
<th>Compound</th>
<th>NaCl</th>
<th>CaCl₂</th>
<th>KCl</th>
<th>Glucose</th>
<th>NaHCO₃</th>
<th>MgCl₂.6H₂O</th>
<th>Na₂HPO₄.2H₂O</th>
<th>KH₂PO₄</th>
<th>MgSO₄.7H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (g.L⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.14</td>
<td>0.4</td>
<td>1</td>
<td>0.35</td>
<td>1</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 2.5 Chemical composition of the Ringer’s solution[177].

<table>
<thead>
<tr>
<th>Compound</th>
<th>NaCl</th>
<th>KCl</th>
<th>CaCl₂</th>
<th>PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (g.L⁻¹)</td>
<td>8.6</td>
<td>0.3</td>
<td>0.33</td>
<td>7.4</td>
</tr>
</tbody>
</table>

2) Corrosion mechanism.

In a biological environment, the most common corrosions are uniform corrosion, galvanic and stress corrosion, as well as pitting and fatigue corrosion [175, 178]. Degradation of Fe-based metallic degradable biomaterials (DBMs) in body fluids is a complex process. A thorough investigation of the corrosion mechanism in the physiological environment is extremely helpful to adjust the degradation rate through modifying the chemical compositions and microstructures of those proposed Fe-based DBMs. Moreover, the mechanical stability of implants is largely determined by the corrosion mechanism. A uniform corrosion, for example, is favourable to the mechanical stability of the implants during serving in the human body.

2.6.1 Corrosion models of Fe in aqueous solution

Corrosion of Fe-based DBMs is usually caused by chemical or electrochemical change in body fluid, and it is followed by a variety of mechanisms, such as galvanic corrosion, stress corrosion, pitting corrosion and intergranular corrosion, etc. [179]. In past few years, several corrosion models have been developed to reveal and explain the corrosion mechanism of Fe-based DBMs and the formation of their corrosion products in body fluids. Based on the corrosion products on the surface of pure Fe immersed in Hank’s solution, M. Moravej et al. established a corrosion model of pure Fe DBMs [180]. Firstly, iron was oxidized in the form of positively charged Fe²⁺ as given by Eqs. (2.1) and (2.2), Meanwhile, as shown in Eq. (2.3),
the positively charged Fe$^{2+}$ reacted with negatively charged hydroxyl ions and led to the formation of ferrous hydroxide.

Anodic reaction \[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \] (2.1)

Cathodic reaction \[ \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow OH^- \] (2.2)

Product formation \[ Fe^{2+} + OH^- \rightarrow Fe(OH)_2 \] (2.3)

Part of ferrous ions (Fe$^{2+}$) on the surface were further oxidised to ferric ions (Fe$^{3+}$). Then, the ferric hydroxide (Eq. (2.5)) was formed under the environment of Hanks’ solution.

\[ Fe^{2+} \rightarrow Fe^{3+} + e^- \] (2.4)

\[ Fe^{3+} + OH^- \rightarrow Fe(OH)_3 \] (2.5)

As the physiological system contains many aggressive ions such as Cl$^-$, HPO$_4^{2-}$, HCO$_3^-$, SO$_4^{2-}$, it was also suggested that some of the ferric hydroxide may be hydrolysed into goethite (α-FeO(OH)). Goethite then reacted with ferrous hydroxide and form magnetite, as given by Eq. (2.6).

\[ Fe(OH)_2 + 2FeO(OH) \rightarrow Fe_3O_4 + H_2O \] (2.6)

Another more comprehensive model was designed to illustrate the degradation behaviour of the binary Fe-Mn DBMs [20]. In this model, the corrosion process was considered to involve four steps, including initial corrosion reaction, formation of hydroxide layer, formation of pits as well as formation of calcium/phosphorus layer. The schematic diagram of corrosion mechanism for Fe-Mn alloys is shown in Figure 2.9 [20]. In the first stage, Fe$^{2+}$, Mn$^{2+}$ and OH$^-$ were formed after the Fe-Mn samples were soaked in modified Hank’s solution.

\[ Fe \rightarrow Fe^{2+} + 2e^- \] (2.7)

\[ Mn \rightarrow Mn^{2+} + 2e^- \] (2.8)
In the second stage, Fe$^{2+}$ reacted with OH$^-$ to form insoluble hydroxides, as shown in Eq. (2.10). According to the surface examination on the corroded Fe-Mn specimens, the substances of the corroded layer consisted of a mixture Fe$_2$O$_3$, Fe$_3$O$_4$ and FeO layers. Therefore, the corrosion process in this stage can be expressed by Eq. (2.11).

$$2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2, or 2FeO \cdot 2H_2O$$  \hspace{1cm} (2.10)

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3, or 2Fe_2O_3 \cdot 6H_2O$$  \hspace{1cm} (2.11)

In the third stage, as the degradation process continues, Cl$^-$ ions in the body fluid reacts with Fe$^{2+}$ to form metal chloride, which was further hydrolysed by water and generated hydroxide and free acid (See Eq.(2.12)). The formation of HCl contributed to the growth of the localised pits.

$$Fe^{2+} + 2Cl^- \rightarrow FeCl_2 + H_2O \rightarrow Fe(OH)_2 + HCl$$  \hspace{1cm} (2.12)

Finally, in the last stage, a new biocompatible layer comprised of calcium/phosphorus is formed on the surface of the implanted medical devices.
Figure 2.9 Degradation model for Fe–Mn alloys: (a) initial corrosion reaction, (b) formation of hydroxide layer, (c) formation of pits, and (d) formation of Ca/P layer [20].

2.6.2 Degradation rate of Fe and its alloys

Fe-based DBMs were first reported in 2001 [53]. Stents made of cast pure iron were implanted both in vitro and in vivo (descending aorta of New Zealand white rabbits) to determine the feasibility of pure Fe applied as DBMs. In this paper, in vitro degradation behaviour of pure iron stents was evaluated in Ringer’s solution for two weeks under continuous stirring at 37°C. Figure 2.10 shows detailed data on iron ion concentration in Ringer’s solution as a function of immersion time. Results revealed that iron ion concentration increased steadily with the increase of soak time, and the average degradation rate of iron in vitro was \(\sim 1697 \text{ g/} (\text{m}^2 \times \text{h})\) during a 2-week immersion test. However, in vivo study implied that the degradation rate of pure iron stents was too slow. It was suggested that employing alloying element, as well as modifying the surface was necessary in order to
obtain a desirable degradation rate of Fe-based DBMs. In 2006, a similar investigation was performed by a research group in Germany[181]. In this study, stents (See Figure 2.11) produced by cast pure iron were implanted into the descending aorta (See Figure 2.11) of 29 pigs with a period of up to 12 months. A general conclusion was that large parts of fragmented pure iron stents remained in the wall of the stented vessel after a 12-month implantation (see Figure 2.12). This again proved that the degradation performance of pure iron stents cannot meet the requirement of clinical application.

Figure 2.10 Accumulation of iron in Ringer’s solution as a function of time[53].

Figure 2.11 Stented descending aorta of a minipig (Note: the stent site was marked with an asterisk)[181].
Figure 2.12 Implanted pure Fe stents in the inner wall of the descending aorta of pigs after 3 months (a), 6 months(b) and 12 months(c) implantation [181].

To improve the degradation performance of pure iron DBMs, a novel technique, electroforming, was employed to fabricate pure iron foil with fine microstructure [180]. The corrosion rate of electroformed Fe (E-Fe) was compared to those produced by casting and thermomechanical treatment Fe (CTT-Fe). Table 2.6 indicates that the degradation rate of E-Fe was significantly higher than their CTT-Fe counterparts. It was found that the fine microstructure of E-Fe contributed to the improvement of the degradation rate.

Table 2.6 Corrosion rate of different cardiovascular stent materials [180].

<table>
<thead>
<tr>
<th>Materials</th>
<th>(i_{corr}) (μA cm(^{-2}))</th>
<th>Corrosion rate (Mm year(^{-1}))</th>
<th>Corrosion potential (mv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-Fe</td>
<td>73.4</td>
<td>0.85</td>
<td>-824</td>
</tr>
<tr>
<td>CCT-Fe, annealed</td>
<td>14</td>
<td>0.16</td>
<td>-732</td>
</tr>
<tr>
<td>Fe-35Mn alloy</td>
<td>36.6</td>
<td>0.44</td>
<td>-740</td>
</tr>
<tr>
<td>AM60B-F Mg alloy</td>
<td>406</td>
<td>2.78</td>
<td>-1750</td>
</tr>
</tbody>
</table>
Adding alloying elements to pure iron is another attempt to promote the degradation rate of Fe. Hermawan et al. were the first to study the feasibility of Fe-based alloys proposed as degradable biomaterials [21, 127, 182, 183]. In Hermawan’s study, manganese (Mn) was selected as the alloying element to synthesis Fe-based DBMs due to a reasonable biocompatibility of Mn. Binary Fe-Mn alloys with four compositions (Fe-20wt.%Mn, Fe-25wt.%Mn, Fe-30wt.%Mn, and Fe-35wt.%Mn) were produced by the PM technique. A repeated rolling-sintering step (Figure 2.13) was carried out to achieve the desired microstructure and mechanical properties. The measured degradation rate of Fe-Mn alloys is available in Table 2.7. It was revealed that all the sintered Fe-Mn alloys exhibited a much higher degradation rate than cast pure iron. Moreover, the results also suggested that the sintered Fe-Mn alloys comprised of a duplex γ-austenite and ε-martensite phase presented a higher corrosion rate compared to one that only had a single γ-austenite or ε-martensite phase.

![Fabrication process of Fe-Mn alloys](image)

Figure 2.13 Fabrication process of Fe-Mn alloys [21, 127, 182, 183].
Table 2.7 Corrosion rate (CR) of Fe-Mn alloys in comparison [127].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Icorr (μA cm⁻²)</th>
<th>CR (mm/year⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quenched</td>
<td>Cold rolled</td>
</tr>
<tr>
<td>Fe-20Mn</td>
<td>113</td>
<td>39</td>
</tr>
<tr>
<td>Fe-25Mn</td>
<td>91</td>
<td>40</td>
</tr>
<tr>
<td>Fe-30Mn</td>
<td>56</td>
<td>57</td>
</tr>
<tr>
<td>Fe-35Mn</td>
<td>37</td>
<td>55</td>
</tr>
<tr>
<td>Pure iron</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.14  Mass loss over immersion time of Fe, Fe–10Mn and Fe–10Mn–1Pd alloys [36].
Based on binary Fe-Mn alloys, several ternary alloys such as Fe-Mn-Pd and Fe-Mn-Si alloys were developed [36, 184, 185]. The aim of this design was to offer the new ternary DBMs with higher degradation rate and mechanical properties compared to the existing binary Fe-Mn DBMs. Pd, for example, was expected to generate a dispersed intermetallic phase that acted as a cathode with respect to the Fe matrix in the ternary Fe-Mn-Pd alloys. Figure 2.14 shows that the degradation rate of the newly developed Fe–10wt.%Mn–1wt.%Pd alloy was one order of magnitude higher than that of pure Fe and Fe-10wt.%Mn alloy. In addition, Fe-10wt.%Mn-1wt.%Pd alloys exhibited significantly higher mechanical performance (See Table 2.7). This reveals that the addition of Pd can effectively promote the degradation performance of the ternary Fe-Mn-Pd alloy. Liu et al. investigated Fe-30Mn-6Si as a type of degradable biomaterial [38]. Traditionally, Fe-Mn-Si alloys are regarded as promising shape memory alloys. Liu’s assessment reveals that Fe-Mn-Si alloys presented higher degradation rates compared to their binary Fe-Mn counterparts.

2.7 Biocompatibility of Fe-based DBMs

In addition to suitable mechanical properties and degradation rate, desirable degradable biomaterials should also present reasonable biocompatibility in the human body. Therefore, biocompatibility assessment of designed degradable biomaterials both in vitro and in vivo is a critical issue that must be carefully conducted as harmful interactions between degradable implants and the host tissue are inevitable [186-188]. A degradable biomaterial is supposed to be biocompatible when it fulfills the following criteria [189, 190]: (a) biosafety, i.e., appropriate host response (no acute inflammatory response/physical irritation) as well as low cytotoxicity, and (b) bio-functionality, i.e. the ability of implantable biomaterials to perform a specific task depending on applications. General principles and biocompatibility test categories of biodegradable implants are detailed in Table 2.8 and Table 2.9, respectively [134, 191].
2.7.1 In vitro biocompatibility testing of Fe-based DBMs

In vitro biocompatibility testing of Fe-based biomaterials is an essential step before proceeding to in vivo studies. In vitro biocompatibility testing can provide preliminary data on a specific candidate, from which researchers can determine whether it is necessary to carry out further in vivo testing for Fe-based biomaterials[192]. Moravej et al. assessed the in vitro
cytotoxicity of E-Fe [180]. The investigation was carried out in rat smooth muscle cells. The results in Figure 2.15 revealed that electroformed Fe discs had no significant inhibition effect on the cell metabolic activity during a period of 72 h incubation.

Figure 2.15  Cell viability of pure iron and 316L SS: the columns illustrated the cell metabolic activities as a function of incubation time (left axis), while the curve is the total cell count (right axis) [180].

Fe-Mn alloys are considered as one of the most promising candidates to be applied as degradable biomaterials. To evaluate the biocompatibility of those proposed Fe-Mn biomaterials, an in vitro cytotoxicity study was carried out by Hermawan et al [20]. Figure 2.16 suggested that the metabolic activity of 3T3 fibroblast cells exposed to Fe-35Mn alloy decreased gradually with the increase of the ion concentration from Fe-35Mn alloy. The relative metabolic activities became zero when the ion concentration from Fe-35Mn alloy reached 16mg.ml\(^{-1}\). This reveals that an excessive high ion concentration of Fe-35Mn alloy can be detrimental to the human body. In B Liu’s work, six binary alloys with 97 at.% iron (in atomic percentage) and 3 at.% alloying element X (Mn, Co, Al, W, Sn, and B) were prepared to assess the biocompatibility of the alloying elements [193]. It was found that all
alloying elements in Fe–X binary alloys decreased the viability of the L929 cells, but none of alloying elements significantly declined the viability of smooth muscle cells. In addition, it was also suggested that the hemolysis percentage of all Fe-X binary alloys was very low (≤5%) during the in vitro experimental period.

Figure 2.16 The effect of various metal powders on relative metabolic activity of 3T3 fibroblast cells: (a) Cell viability as a function of concentration of different types of powders, (b) Cell viability at a fixed concentration (0.5 mg·ml⁻¹). (Note: Fe+Mn is powder mixture of 65wt.% of Fe combined with 35wt.% of Mn) [20].
2.7.2 In vivo biocompatibility tests of Fe-based DBMs

The in vivo biocompatibility of Fe-based DBMs has been evaluated by implanting pure iron stents in the vessels of rabbits since 2000 [53]. The in vivo study indicated that pure iron DBMs present a reasonable biocompatibility. This was because all subjects survived during a trial period up to 18 months with no pronounced neointimal proliferation, inflammatory or thrombosis. In addition, histopathological evaluation of the rabbits’ organs reveals that accumulation of the degradation products and systemic toxicity in the organs was not observed. A similar long-term biocompatibility assessment of pure iron DBMs was performed in the descending aorta of pigs [181]. This again demonstrated pure iron is a suitable candidate for degradable cardiovascular stents in terms of in vivo biocompatibility. In addition to the long-term biocompatibility evaluation of iron DBMs, short-term biocompatibility evaluation was performed in vivo as well.
Waksman et al. conducted a short-term in vivo experiment to evaluate both the biocompatibility and mechanical stability of pure iron stents [194]. Prepared stents were placed in the left carotid artery of eight pigs for 28 days. In addition, stents made of Co-Cr alloy were implanted into the vessels of pigs for comparison purposes. X-ray radiographs showed that the pure iron stent struts were distorted compared to their Co-Cr counterparts (Figure 2.19) because of the lower mechanical properties of pure Fe. However, it was concluded that pure iron stents were better than their Co-Cr counterparts in terms of biocompatibility. This is because the intimal thickness, intimal area, percentage occlusion and inflammation were less in the areas placed with the pure iron stents compared to those implanted with Co-Cr stents. It was noted that localised brown tissue (Figure 2.18) was observed on the vascular walls around the pure iron stents. Analysis indicated that the brown tissue was caused by the absorption of degradation products.

Figure 2.18  Micrographs of stented sections of porcine arteries after implanting iron and Co-Cr stents for 28 days [194].
Figure 2.19  X-ray photographs of the stents: (a) pure Fe, (b) Co-Cr alloys in porcine coronary arteries[194].

The latest study on the in vivo biocompatibility of pure iron DBMs was carried out by a research group in Germany. In this study, pure iron foils with a size of 5 mm×5 mm×0.5μm were implanted into the tails of mice (See Figure 2.20 and Figure 2.21 for details) [195]. Figure 2.20 illustrated that the surface of the pure iron foil partially corroded after a one month short term implantation. In order to monitor the degradation process of the pure iron foil in situ, micro-computed tomography (micro-CT) was employed to observe the foils in the tails of the mice. The micro-CT observation (Figure 2.22) demonstrated that the foils started losing their integrity 6 months after implantation and further fragmented to several granular pieces 9 months later. In additional, histological and gene expression data indicated that the degradation products only presented limited inflammatory and toxic effects on the mice.

Figure 2.20 Corrosion of pure iron foil. (A) rolled iron foil before implantation, (B) foil implanted in the mouse tail after one month [195].
Figure 2.21  Implantation procedure of pure iron foil in a mouse tail. (A) Square with area of 5x5 mm wrapped as a roll; (B) An intravenous catheter was inserted at the site of the tail vein of an anaesthetized mouse; (C) The pure iron roll was placed using a guide wire; (D) the intravenous catheter was pulled out [195].

Figure 2.22  Degradation of pure iron foil rolls in mouse tails observed by a computed tomogram (CT) after implantation: (A) cross-section of the implanted pure iron roll, (B) implanted for 1 month at longitudinal direction, (C) implanted for 3 months, (D) 6 months, and (E) 9 months after implantation [195].
2.8 Summary

Over the past few decades, degradable biomaterials have become promising candidates to replace their corrosion-resistant counterparts in temporary implants such as stents and bone fixation devices. Fe and its alloys have been intensively investigated among all the proposed degradable biomaterials due to its low cost of the raw materials, good mechanical properties, degradability and reasonable biocompatibility. According to the literature review above, the following can be summarised.

In general, Fe-based alloys can be fabricated by either PM or casting. PM is a preferred route to fabricate Fe-based alloys as degradable biomaterials compared to casting. This is because PM is regarded as an effective way to control and tailor the porosity of Fe-based alloys. The porosity in the PM Fe-based alloys is beneficial to improve the degradation rate.

Fe-based alloys are designed to be proposed as materials for temporary load-bearing implants. Currently, the application of Fe-based alloys as DBMs is impeded by their low degradation rate. A variety of attempts such as modification of the composition, addition of alloying elements as well as the application of new manufacturing methods, have been performed to improve the degradation rate of Fe-based alloys.

Sublimation/evaporation of Mn in Fe-Mn-based alloys/steels is a critical issue that must be considered during the fabrication of Mn alloys at high temperatures due to the high vapour pressure of Mn. So far, most reports on the sublimation of Fe-Mn-based alloys/steels have focused on casting/wrought alloys with low Mn content. By contrast, the work on the sublimation/evaporation of PM Fe-Mn-based alloys is still limited. Thus, it is our interest to find out how PM parameters (sintering temperature, sintering time and particle size of starting powers) affect the sublimation/evaporation of Mn in PM Fe-Mn-based alloys.

Published data reveals that the mechanical properties of Fe-based degradable biomaterials are more competitive compared to their Mg-based or polymer-based counterparts. However, there is still a lack of data on how mechanical properties of Fe-based degradable biomaterials would be changed as a function of time when samples are continuously exposed in the physiological environment.
Both in vitro and in vivo studies demonstrated pure Fe is suitable to be used as biodegradable implants in terms of biocompatibility. However, pure iron DBMs presented a low degradation rate which is far away from meeting the requirement for applications of temporary implants. In this case, adding alloying elements into the Fe matrix has become an option to accelerate the degradation rate of Fe-based DBMs. Fe-Mn-Si alloys have preliminarily proven to be promising candidates for degradable biomaterials. The newly developed Fe-Mn-Si DBMs were fabricated by the traditional casting/wrought route. In other words, no investigation on PM Fe-Mn-Si alloys as degradable biomaterials was scientifically reported. Thus, it makes sense to study the degradation performance of the PM Fe-Mn-Si alloys as degradable biomaterials, and compare them to those fabricated by the cast/wrought route.
Chapter 3  Experimental setup and procedures

3.1  Raw materials

3.1.1  Materials for casting

The raw materials used for casting were electrolytic Fe (Taiyuan Iron & Steel Co., Ltd, China) with purity of 99.9% in wt.%, electrolytic Mn (Xiangyu Foundry Materials Co., Ltd, China) with purity of 99.7 in wt.% and Fe75Si master alloys (Star Metallurgy Materials Co., Ltd, China). The macrographs of raw materials are shown in Figure 3.1. The chemical composition of the raw materials is listed in Table 3.1, Table 3.2 and Table 3.3, respectively.

Figure 3.1  Macrographs of Fe (a), Mn (b) and Fe75Si (c).
Table 3.1 Compositions of electrolytic Fe chips (in wt.%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>&gt;99.9</td>
<td>0.0015</td>
<td>0.008</td>
<td>0.02</td>
<td>0.005</td>
<td>0.005</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 3.2 Compositions of electrolytic Mn chips (in wt.%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Mn</th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>&gt;99.7</td>
<td>≤0.04</td>
<td>≤0.05</td>
<td>≤0.005</td>
<td>≤0.001</td>
</tr>
</tbody>
</table>

Table 3.3 Compositions of Fe75Si master alloy (in wt.%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Fe</th>
<th>Ca</th>
<th>Al</th>
<th>Ti</th>
<th>Ba</th>
<th>Mg</th>
<th>Mn</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>77.95</td>
<td>18.23</td>
<td>1.63</td>
<td>1.5</td>
<td>0.2</td>
<td>0.15</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
</tr>
</tbody>
</table>

3.1.2 Materials for powder metallurgy

The starting powders used in this study were pure elemental Fe powder, Mn powder and Si powder. The chemical purity and particle size are listed in Table 3.4, while the morphologies of these powders are shown in Figure 3.2. Figure 3.2 reveals that all these starting powders were of angular shape. The XRD results of the starting powders are shown in Figure 3.3.

Table 3.4 Particle size and impurities of the starting powders.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Particle Size (μm)a,b</th>
<th>Impurities (wt.%c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d_{10}</td>
<td>d_{50}</td>
</tr>
<tr>
<td>Fe</td>
<td>19.96</td>
<td>38.62</td>
</tr>
<tr>
<td>Mn</td>
<td>14.91</td>
<td>38.7</td>
</tr>
<tr>
<td>Si</td>
<td>18.17</td>
<td>43.41</td>
</tr>
</tbody>
</table>

a, b  $D_{10}$, $D_{50}$, $D_{90}$ correspond to the particle sizes at the 10, 50 and 90 percentiles on the cumulative distribution.

b  The particle size is determined by a particle size analyser (Mastersizer-2000, Malvern Instruments Ltd, UK).

c  The oxygen is determined measured by an oxygen elemental analyser (ONH836, Leco, USA) The carbon and nitrogen content is measured by a CN elemental combustion analyser (Carlo-Erba NA 1500, Thermo Scientific, USA).
Figure 3.2 Morphologies of the as-received starting powders (a) Fe, (b) Mn and (c) Si.
3.2 Powder preparation

3.2.1 Mechanical milling

In this project, two types of powder mixtures were prepared. One is blended elemental (BE) powder mixture; the other is mechanical milled (MM) powder mixture. The BE powder mixtures were simply prepared by mixing the powders for 10 h in a tubular blender. It is noted that the BE process was undertaken by a gentle mixing to obtain a homogeneous distribution. The adoption of 10 h blending is based on the previous experiment (The powder mixtures were also blended for 2 h and 5 h before a 10 h blending was finally adopted. The results revealed that both 2 h and 5 h blending were not enough to obtain powder mixtures with homogeneous distributions. However, 10 h blending can obtain powder mixtures with more homogeneous distribution of powder particles compared to 2 h and 5 h blending). In other words, the morphology and the particle size still remain the same as the raw powder. In order to decrease the particle size of the BE powder mixtures, MM was performed. The MM process was carried out in a planetary ball mill. A stainless steel vial and stainless steel balls with a diameter of 6 mm were used. The ball-to-powder weight ratio was 5:1. The powder
mixture was mechanically milled for 5 h with the vial being rotated at 275 rpm. No lubricant was added in the powder mixtures during MM.

### 3.2.2 Powder compaction

After mixing or mechanical milling, the BE or/and MM powder mixtures were then pressed into green compacts under a pressure of 400 MPa at room temperature. Several single-action steel dies with different sizes were employed and are detailed in corresponding chapters.

### 3.3 Fabrication of Fe-Mn-Si alloys

#### 3.3.1 Melting

The cast alloys were prepared using an arc-melting furnace equipped with a non-consumable tungsten electrode. The electrolytic Fe chips (99.9 wt% purity), electrolytic Mn flakes (99.9% purity) and Fe-75wt.%Si master alloys were charged in a water-cooled copper crucible and the chamber was then evacuated to ~ 5×10⁻³ Pa. Then argon (Ar) with high purity of 99.99% was purged in the vacuum chamber with a pressure of 0.08 MPa as a shielding gas against oxidation. Once the Ar was filled, a piece of pure titanium (Ti) was melted before melting Fe-Mn-Si alloys in order to absorb any possible O₂ left in the vacuum chamber. The solidified Fe-Mn-Si button sample was re-melted three times to ensure chemical homogeneity. The macroscopical aspect of a typical as-cast Fe-Mn-Si alloy is shown in Figure 3.4; the weight of the fabricated alloys was about 70g.

![Figure 3.4 Macroscopical image of as-cast Fe-Mn-Si alloys.](image_url)
3.3.2 Powder Sintering

The second type of sample was prepared by the powder metallurgical route. All the green compacts were sintered in a vacuum furnace at ~ 5×10⁻³Pa. The heating rate was 10 °C/min before the temperature (T) reached 800 °C and 5 °C/min from 800 °C to the final sintering temperature. The final sintering was carried out in a wide range of temperatures between 1000 °C and 1300 °C, depending on the specific purpose of the investigation in the following chapters. The isothermal holding time at final sintering temperatures also varied and will be described in relative chapters.

3.4 Characterisation and testing

3.4.1 Morphologic and structural characterisation

The morphologies of all specimens were observed using an optical microscope (Olympus BX60M) and a scanning electron microscope (ESEM, FEI Quanta 200F) equipped with an X-ray energy dispersive spectrometer (EDX). Semi-quantitative compositional analysis was carried out using EDX. Phase identification was conducted on an X-ray diffractometer (Bruker, D2 Phaser) with Cu Kα radiation (λ = 1.54 Å) at room temperature. Before microstructural observation, specimens were ground with 120, 240, 500 and 1200 grit silicon carbide papers, followed by mechanical polishing with 6, 3, 1μm diamond solutions sequentially.

3.4.2 Density

Open porosity and density of the sintered specimens were measured according to the ASTM B962-13 standard. Densities of the forged fully dense samples were measured to be 7.71 g/cm³ for Fe-28Mn, 7.66 g/cm³ for Fe-28Mn-1Si, 7.59 g/cm³ for Fe-28Mn-2Si, 7.50 g/cm³ for Fe-28Mn-3Si, and 7.43 g/cm³ for Fe-28Mn-4Si, and were used as the theoretical densities for calculating relative density of the PM alloy samples. Powder densification (ψ) is calculated by \( \psi = \frac{(\rho_s - \rho_o)}{(1 - \rho_o)} \), where \( \rho_s \) is relative sintered density and \( \rho_o \) is relative green density.
3.4.3 Mechanical testing

Dog-bone shaped flat tensile specimens designed according to ASTM-E8-13 were cut from both as-sintered and cast samples. The test-pieces had a cross section of $1.6 \text{ mm} \times 2 \text{ mm}$ and a gauge length of 8 mm. Tensile tests were carried out on an Instron 3367 universal testing machine with a cross-head speed of 0.2 mm/min at room temperature. The equivalent strain rate is $4.2 \times 10^{-3} \text{ s}^{-1}$.

3.4.4 Electrochemical measurement

Potentiodynamic polarization testing was employed to evaluate the degradation performance of the sintered/cast alloys. A three-electrode cell and a CHI604D (Chenhua, Shanghai) electrochemical workstation were used for the electrochemical measurements in a simulated body fluid (SBF) solution [196] according to the ASTM-G59 standard. The specimens, a platinum electrode (Size: $2 \text{ cm} \times 2 \text{ cm} \times 0.05 \text{ cm}$) and a saturated calomel electrode (SCE) were chosen as the working, auxiliary, and reference electrodes, respectively. The specimens were ground with SiC sand paper up to 1200 grit and rinsed with ethanol. The surface area of the specimens exposed to the SBF solution was $1 \text{ cm} \times 1 \text{ cm}$. Linear scanning voltammograms were recorded at a scan rate of 5 mV/s from -1.3 to -0.5 V.

Table 3.5 The weight of chemicals for preparing 1000 ml SBF solution[196].

<table>
<thead>
<tr>
<th>Order</th>
<th>Reagent</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl</td>
<td>8.035 g</td>
</tr>
<tr>
<td>2</td>
<td>NaHCO$_3$</td>
<td>0.355 g</td>
</tr>
<tr>
<td>3</td>
<td>KCl</td>
<td>0.225 g</td>
</tr>
<tr>
<td>4</td>
<td>K$_2$HPO$_4$·3H$_2$O</td>
<td>0.231 g</td>
</tr>
<tr>
<td>5</td>
<td>MgCl$_2$·6H$_2$O</td>
<td>0.311 g</td>
</tr>
<tr>
<td>6</td>
<td>1.0M-HCl</td>
<td>39 ml</td>
</tr>
<tr>
<td>7</td>
<td>CaCl$_2$</td>
<td>0.292 g</td>
</tr>
<tr>
<td>8</td>
<td>Na$_2$SO$_4$</td>
<td>0.072 g</td>
</tr>
<tr>
<td>9</td>
<td>Tris*</td>
<td>6.118 g</td>
</tr>
<tr>
<td>10</td>
<td>1.0M-HCl</td>
<td>0-5 ml</td>
</tr>
</tbody>
</table>

*Tris-hydroxymethyl aminomethane ((HOCH$_2$)$_3$CNH$_2$).
Figure 3.5 Schematic set-up of a three-electrode cell system: working electrode (1), auxiliary electrode (2) and reference electrode (3).

3.5 Cytotoxicity assessment

Murine fibroblast cells (L-929) were employed to assess the cytotoxicity of Fe-Mn-Si alloys, and were cultured at 37 °C in a humidified atmosphere of 5% CO₂. The medium for L-929 cells culture was Dulbecco’s Modified Eagle Medium (DMEM) (Gibco), supplemented with 10% foetal calf serum (FCS). The cell viability was tested by an indirect contact method. After 72 h incubation, the cultured cells were diluted to a concentration of 2x10⁴ cells/ml using DMEM media. Then, 1 ml of the diluted cells was placed into each well of a 24-well plate. 1ml of fresh DMEM medium was also placed into 3 wells of the 24-well plate, which was used as control in this study. The plate seeded with cells was incubated for 24 h at 37 °C in 5% CO₂ for cell attachment.

Resazurin fluorescence assay was used to determine the cell proliferation during the testing. Samples for cytotoxicity testing were immersed with bulk Fe-Mn-Si samples in SBF solution. After 24 h, 1ml of 500 μM resazurin was placed into each well of the plate to replace the cell
medium/ DMEM. The plate was incubated for 4 h, and then the supernatant in each well was collected and centrifuged at 2000 rpm for 5 min at room temperature. 100 μL of the centrifuged supernatant was placed in triplicate into a 96-well flat bottomed cell culture plate and the fluorescence value was recorded at 530 nm excitation and 590 nm emission using a Perkin Elmer Enspire 2300 Multibabel Reader. The cells without supernatant in each well were washed using 1 ml of phosphate buffered saline (PBS). Subsequently, 800 μl of fresh DMEM medium and 200 μl of sample solution were added into each well of the plate. For the control group, 1ml of fresh DMEM medium was added. After this, the 24-well plate was returned to incubator overnight for cell growth. The above procedure was repeated daily in the following four days. The entire procedure of the testing was repeated for three times.
Chapter 4 Weight loss behaviour of vacuum sintered powder metallurgical Fe-Mn-Si alloys

4.1 Introduction

Fe-Mn-Si alloys have attracted extensive attention over the past three decades, as they are promising materials for civil applications, such as pipe joints and dampers due to their unique shape memory effect, good damping capacity and low cost over other shape memory alloys (SMAs) [197-201]. Recent research reveals that Fe-Mn-Si alloys are a type of potential degradable biomaterial used for cardiovascular stents, because of their good biocompatibility, degradability, high mechanical performance and low hemolysis percentage [38, 202, 203]. Traditionally, Fe-Mn-Si alloys are fabricated by casting, followed by a series of thermomechanical treatments. To date only few publications have reported on the fabrication of Fe-Mn-Si shape memory alloys using powder metallurgy (PM). This is because with PM routes it is difficult to achieve fully dense alloys, and the presence of porosity may affect the shape memory effect and mechanical properties of these alloys. However, the presence of porosity may not be always adverse; in some cases the porous microstructure is preferable because the porous biodegradable materials exhibit a few advantages. Firstly, the pores in P/M Fe-Mn-Si alloys give rise to a higher degradation rate, as compared to their pore-free counterparts prepared by casting because of the larger surface area created by the pores. Secondly, the mechanical and physical properties, such as strength and stiffness can be adjusted via the amount of porosity and the pore characteristics.

According to the Ellingham diagram [204], both alloying elements Mn and Si exhibit high sensitivity to oxygen. Sintering Fe-Mn-Si alloys under high vacuum is one of the solutions to prevent the reaction of Mn and Si with oxygen. However, the sublimation of Mn during sintering Fe-Mn-Si alloys with high Mn concentration (≥ 20 wt.%) in vacuum is an issue that cannot be neglected, as Mn presents a high vapour pressure at high sintering temperatures [118]. The sublimation of Mn may affect the composition of the sintered Fe-Mn-based alloys, and hence their mechanical and corrosion properties. Therefore, it is important to investigate the sublimation behaviour of Mn in Fe-Mn based alloys during vacuum sintering and the resulting microstructure in the sintered compacts. In this paper, the
ternary Fe-28Mn-3Si (wt.%) powder mixtures were sintered at different temperatures under 5x10^{-3} Pa. It is noted that the selection of the composition of Fe-28wt.%Mn-3wt.%Si was determined by combined considerations of mechanical properties and degradation performance. The details are presented in Chapter 7. In this chapter, we compared, for the first time, the mass loss of the sintered Fe-Mn-Si compacts with high Mn content (≥20 wt.%). In addition, we discussed the effects of mechanical milling (MM) and sintering temperature on the sublimation behaviour of Mn in the sintered compacts.

### 4.2 Calculation of activity and partial pressure

Activity and partial pressure are key parameters to evaluate the sublimation of the alloying elements, especially the sublimation of Mn in the Fe-Mn-Si alloys during vacuum sintering. The calculation of the activity and partial pressure of each alloying element in the ternary system is shown as follows.

The activity of element $i$ (denoted as $a_i$) is directly related to chemical potential, and is described as:

$$a_i = \exp \left( \frac{\mu_i - \mu_i^0}{RT} \right) \tag{4.1}$$

Where $\mu_i$ is the chemical potential of $i$ in a certain state, $\mu_i^0$ is the chemical potential of $i$ in the standard state, $R$ is the gas constant, $T$ is the temperature in Kelvin. Therefore, the activity is 1 for a pure element in the standard state.

The chemical potential of element $i$ is calculated from the Gibbs energy equation:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j(j \neq i)} \tag{4.2}$$

where the temperature (T), pressure (P) and composition of other elements are constants.
At equilibrium, $\mu_i$ is the same value for all the phases. For instance, the following relationship is fulfilled for three-phase equilibrium ($\alpha+\beta+\gamma$ phases) in a ternary A-B-C system:

$$
\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma
$$

(4.3)

The Gibbs energy of a solution phase ($\phi$) in a ternary A-B-C system can be described by the Redlich–Kister polynomial [205]:

$$
^{0}G_{m}^{\phi} = x_A^{0}G_A^{\phi} + x_B^{0}G_B^{\phi} + x_C^{0}G_C^{\phi} + RT(x_A\ln x_A + x_B\ln x_B + x_C\ln x_C) + x_Ax_BL_{A,B}^{\phi} + x_Bx_CL_{B,C}^{\phi} + x_Ax_CL_{A,C}^{\phi} + ^{0}G_{A,B,C}^{\phi} + ^{\Delta}G_{mag}
$$

(4.4)

where $x_i$ is the molar fraction of element $i$, $^{0}G_i^{\phi}$ is Gibbs energy at the standard state, the terms $L_{i,j}^{\phi}$ ($i, j = A, B, C$) are the interaction parameters from the binary systems, $^{0}G_{A,B,C}^{\phi}$ is the excess Gibbs energy and $^{\Delta}G_{mag}$ is the magnetic contribution to the Gibbs energy.

The Gibbs energies of all phases in the ternary Fe-Mn-Si system have been determined using the CALPHAD method [206] in Ref.[207]. These data were used to calculate the activities of Fe, Mn, Si of the ternary Fe-Mn-Si alloys in this work.

The sublimation rate of an element in the alloy is determined by its partial pressure ($P_i^\ast$), as:

$$
P_i^\ast = a_i \cdot P_i
$$

(4.5)

Where $P_i$ is the equilibrium vapour pressure of a pure element $i$. The values of $P_{Fe}, P_{Mn}$ and $P_{Si}$, as a function of temperature, are given in the following three relations [208].

$$
\log P_{Fe} = 12.106 - 21723 / T + 0.4536 \log T - 0.5846 / T^3
$$

(4.6)
\[
\log P_{\text{Mo}} = 17.811 - 15097 / T - 1.7896 \log T \tag{4.7}
\]

\[
\log P_{\text{Si}} = 12.325 - 19720 / T \tag{4.8}
\]

### 4.3 Experimental

Three elemental powders were selected as the starting materials in this study: Fe (99.9% purity), Mn (99.7% purity) and Si (99.95% purity). XRD patterns (Figure 3.3) reveal that all powders presented a single phase. The mean particle sizes of Fe, Mn and Si powders are 38.6, 38.7 and 43.4 μm, respectively. The morphologies of these particles are shown in Figure 3.2, where all these three powders exhibited an angular shape.

Powder mixtures with a nominal composition of 69 wt.% Fe, 28 wt.% Mn and 3 wt.% Si were used in this study. Two types of powder mixtures were prepared. One was performed with mechanical milling (MM) for 5h. The MM process was carried out in a planetary ball mill. A stainless steel vial and stainless steel balls with a diameter of 6 mm were used. The ball-to-powder ratio was 5:1. The powder mixture was mechanically milled with the vial being rotated at 275 rpm. The other was a blended powder mixture (BE), which was gently blended for 10 h, without ball milling. Figure 4.1 presents the morphology of both the BE and MM green compacts. As shown in Figure 4.1, the particle size of Mn and Si in the MM powder mixture was reduced to ~5 μm, significantly smaller compared to their BE counterparts (~38 μm). The Fe particles were elongated via mechanical milling (Figure 4.1(b)). The densities of both BE and MM green compacts are shown in Fig. 5.4 (Chapter 5).
Both BE and MM powder mixtures were pressed into cylindrical discs (15 mm in diameter and 3.5 mm in thickness) in a single-action steel die under a pressure of 400 MPa at room temperature. All of these green compacts were then sintered in a high vacuum furnace at 5x10^{-3}Pa. Figure 4.2 illustrates the temperature profile. The heating rate was set at 10°C/min from room temperature to 800°C, and 5°C/min from 800°C to the final sintering temperature. A total of six batches of samples were sintered at three final temperatures 1000°C, 1100°C and 1200°C. In detail, three batches of samples were heated to the final temperatures (1000°C, 1100°C and 1200°C) and terminated without holding; another three batches were further isothermally held for 3h at 1000°C, 1100°C and 1200°C, respectively.
The weight of both the green compacts and sintered compacts was measured with a high precision electronic balance. The weight loss rate is defined as \((m_0 - m_1)/m_0\), where \(m_0\) is the original weight of the green compacts, while \(m_1\) is the final weight of the samples after sintering.
4.4 Results

4.4.1 Weight loss and composition change

Figure 4.3 Weight loss of the Fe-28Mn-3Si compacts sintered at three temperatures for 3h.

Figure 4.3 shows the weight loss of the samples sintered at the three temperatures for 3h. The weight loss of the compacts sintered at 1000°C was low (~2.7%). However, increasing temperature resulted in a significant weight loss. For example, the weight loss of the BE compacts sintered at 1200°C was ~18.95%, ~7-fold higher than that sintered at 1000°C. It is also noted that the weight loss of the BE compacts was much larger than their MM counterparts sintered at the same temperature above 1100°C. For instance, the weight loss of the BE compacts sintered at 1200°C was 18.95%, while that of the MM compacts was approximately 9.25%.
Figure 4.4 Weight loss of the Fe-Mn-Si compacts heated between 1000°C and 1200°C with no isothermal holding.

Figure 4.4 shows the weight loss of the Fe-28Mn-3Si compacts that were heated to the prescribed temperatures but without isothermal holding. As shown in Figure 4.4, the weight loss shows a similar trend to those isothermally held for 3hrs in that the weight loss of the MM compacts was lower than the BE compacts. However, for these compacts with no isothermal holding the weight loss was significantly lower; in all these compacts, the weight loss was no more than 3.7 wt.% at all temperatures. The highest weight loss of ~3.65% was observed in the BE compacts sintered at 1200°C, which was only 1/5 of the BE compacts isothermally held for 3 h at the same temperature. This reveals that the weight loss mainly occurred during the isothermal holding stage.
Figure 4.5 Morphology of the cross-section of the Fe-28Mn-3Si compacts sintered at 1100°C.

To identify the compositional distribution of Fe, Mn and Si in the sintered ternary alloys, EDX line scans were conducted on a polished cross-section, as shown in Figure 4.5.

Figure 4.6 presents the Mn and Si line scan profile of the MM compacts sintered at 1100°C for 3h. As shown in Figure 4.6, the Mn content increased parabolically from the surface to the interior of compact, where the Mn content approached ~27 wt.%. The Si content, however, fluctuated at ~ 3.2 wt.% in the same region (Figure 4.6). This demonstrates that an obvious Mn depletion region existed in the sintered compacts. We define the length of this Mn depletion region from the surface to the location where the Mn content reaches its bulk composition as MDR. As shown in Table 4.1, MDR varies with sintering temperature and the characteristics of powder mixture. MDR of both the BE and MM compacts sintered at 1000°C was very small, less than 15μm. When the sintering temperature increased to $\geq$1100°C, both the BE and MM compacts demonstrated temperature-dependent MDR. For example, the MDR value of the BE compacts sintered at 1100 °C and 1200°C was ~650μm and ~1200μm, 43-fold and 80-fold higher than the BE compacts if they were sintered at 1000°C. It is also noted that mechanical milling reduced largely the value of MDR, by comparing the MM compacts to the BE compacts sintered at the same temperature. For instance, the MDR of the 1200 °C sintered MM compacts was approximately 500 μm, only ~40% of their BE compacts.
As shown in Figure 4.6 and Table 4.1, the Mn concentration in all the sintered compacts increased parabolically with the increase of the distance (x) from the surface (x=0) until it stabilized at ~ 27 wt.% when the distance (x) was ≥ MDR. Moreover, the Si concentration was ~ 3.2 wt.% in all the sintered alloys, regardless of the temperature and the distance from the surface. Therefore, the change of Fe concentration in MDR region can be considered as a function of Mn concentration in the ternary Fe-Mn-Si compacts.

Table 4.1 The chemical composition of the ternary Fe-Mn-Si alloys sintered at different temperatures.

<table>
<thead>
<tr>
<th>Powder mixture</th>
<th>Temperature (°C)</th>
<th>Chemical composition on the surface x=0 (wt.%)</th>
<th>MDR (μm)</th>
<th>Chemical composition (wt.%) at positions &gt; MDR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>Si</td>
<td>Fe</td>
</tr>
<tr>
<td>BE</td>
<td>1000</td>
<td>&lt;1.44</td>
<td>&lt;2.85</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>&lt;1.36</td>
<td>&lt;2.88</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>&lt;1.43</td>
<td>&lt;3.12</td>
<td>Bal.</td>
</tr>
<tr>
<td>MM</td>
<td>1000</td>
<td>&lt;1.45</td>
<td>&lt;3.36</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>&lt;1.41</td>
<td>&lt;3.25</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>&lt;1.39</td>
<td>&lt;3.07</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
Figure 4.6 Mn and Si concentration in the cross section of MM Fe-Mn-Si alloys sintered at 1100℃ for 3h.
4.4.2 Phase evolution of Fe-28Mn-3Si compacts

Figure 4.7 XRD patterns recorded at the centre of the sample cross section (Distance (x) ≥ MDR) of the ternary Fe-28Mn-3Si alloys sintered for 3h at different sintering temperatures. (a) BE compact sintered at 1000°C, (b) BE compact sintered at 1100°C, (c) BE compact sintered at 1200°C, (d) MM compact sintered at 1000°C, (e) MM compact sintered at 1100°C, (f) MM compact sintered at 1200°C.
Figure 4.8 XRD results recorded on the surface (x=0) of the ternary Fe-28Mn-3Si alloys sintered for 3h at different sintering temperatures. (a) BE compact sintered at 1000°C, (b) BE compact sintered at 1200°C, (c) MM compact sintered at 1000°C, (d) MM compact sintered at 1200°C.

Figure 4.7 shows the XRD patterns recorded at the centre of the cross section (≥ MDR) of the compacts sintered at 1000, 1100 and 1200 °C for 3h. It is clear that γ-austenite was the predominant phase in all the sintered compacts in addition to a minor ε-martensite phase. An exception was observed in the 1000 °C-sintered BE compacts in which an additional minor Mn₃Si phase was also identified. The surface of both the BE and MM compacts presented a single α-ferrite phase in all of the sintered samples, as shown in Figure 4.8.
4.4.3 Open porosity

Figure 4.9  Open porosities of the Fe-28Mn-3Si compacts sintered from both BE and MM powder mixtures as a function of sintering temperature.

The open porosity, as shown in Figure 4.9, decreased with sintering temperature. Each BE compact had a significantly higher open porosity than its MM counterpart sintered at the same temperature. The sintering temperature had less influence on the open porosity for the BE sintered compacts. For instance, the BE compacts presented an open porosity of ~29% if sintered at 1200°C while 34.5% if sintered at 1000°C. By contrast, the open porosity in the MM compacts largely depended on the sintering temperature. For example, the open porosity decreased drastically from ~25% if the compact was sintered at 1000°C, to only ~ 7.5% if sintered at 1200°C.
4.5 Discussion

4.5.1 Effect of sintering temperature on the weight loss

As shown in Figure 4.3 and Figure 4.4, the weight loss of both the BE and MM compacts increased significantly with the sintering temperature. The composition data summarised in Table 4.1 clearly shows that Mn has been lost via sublimation during sintering. It is then speculated that the weight loss is mainly responsible for the sublimation of Mn. Figure 4.10 shows the compositional profile of the compacts without isothermal holding. The MDR region of the samples without isothermal holding was very small as compared to compacts sintered for 3 h (Figure 4.6 and Table 4.1).

Figure 4.10 Mn and Si concentration in the sintered ternary Fe-Mn-Si alloys with no isothermal holding as a function of distance from the surface at different temperatures.
Langmuir theory describes the sublimation rate of an element [209-211]:

\[ N_i = K_L \cdot \varepsilon \cdot p_i^e \cdot \sqrt{M_i/T} \]  \hspace{1cm} (4.9)

where \( N_i \) is the sublimation rate (g·cm\(^{-2}\)·s\(^{-1}\)) of component \( i \), \( K_L \) is Langmuir constant 4.37 x 10\(^{-4}\), \( \varepsilon \) is the condensation coefficient depending on the materials, for metals \( \varepsilon = 1 \), \( p_i^e \) is the partial pressure (Pa) of element \( i \) in the alloy system, \( M_i \) is the molecular weight (g·mol\(^{-1}\)) of component \( i \), \( T \) is the absolute temperature and \( R \) is gas constant.

Figure 4.11 and Figure 4.12 is the activity (\( a \)) and partial pressure (\( p \)) of Fe, Mn, and Si in the MDR region of the ternary Fe-xMn-3Si as a function of Mn concentration (1 wt.% \( \leq \) Mn \( \leq \) 28 wt.%).

![Activity and partial pressure of Fe, Mn, and Si in ternary Fe-Mn-Si alloys as a function of sintering temperature.](image)

Figure 4.11  Activity of Fe, Mn and Si in ternary Fe-Mn-Si alloys as a function of sintering temperature.
In our case, $K_L$ and $\varepsilon$ are constants. The sublimation rate of element $i$ is therefore a function of sintering temperature, according to Eq. 4.9.
In a porous solid material system, the weight loss via sublimation occurs on both the sample surface \( (x=0) \) and also the walls \( (x > 0) \) of the open pores. We discuss the sublimation occurred on the surface \( (x=0) \) and the open pore walls \( (x>0) \).

Figure 4.13 presents the calculated sublimation rate of each element as a function of sintering temperature. The sublimation rate of all elements increased with sintering temperature. Consequently, the weight loss of all the sintered alloys increased with sintering temperature. However, as shown in Figure 4.13, the sublimation value of each element is significantly different. At a certain temperature, e.g. 1100°C, the sublimation of Mn was 12 times higher than Fe and 10^5 times than Si. Meanwhile, the partial pressure of Mn on the sample surface ranges from ~0.025 Pa to ~0.7 Pa, much higher than the vacuum pressure in the furnace.
This indicates that Mn sublimes almost freely at all sintering temperatures. By contrast, the partial pressure of Si ($<5.9 \times 10^{-6}$ Pa) at all sintering temperatures was three orders of magnitude lower than the vacuum pressure in the furnace. Therefore the sublimation of Si in Fe-Mn-Si alloys was negligible. This is also supported by the data from Table 4.1. As shown in Table 4.1, the Si concentration in the ternary Fe-Mn-Si alloys sintered at all temperatures stabilized at ~3.2 wt.%, which is in agreement with the original Si content (3 wt.%) in the green compacts. As for Fe, the partial pressure of Fe at 1100°C (0.004 Pa), which is merely lower than the furnace pressure (0.005 Pa). This suggests that the sublimation of Fe was significantly suppressed at temperatures $\leq$ 1100°C. At a temperature of 1200°C, the Fe partial pressure was 0.54 Pa, which is slightly higher than the pressure of the vacuum chamber. This reveals that Fe sublimated almost freely in vacuum chamber when sintering at 1200°C. However, considering the high ratio of the evaporation rate of Mn to Fe (~ 12) in ternary system, the sublimation rate of Fe was much lower than Mn. Thus, the weight loss of the ternary Fe-Mn-Si compacts sintered at between 1000°C and 1200°C was mainly caused by the sublimation of Mn. This calculation is in good agreement with the data listed in Table 4.1.

The open pores in the powder compacts are the sublimation sites at high temperatures. As shown in Figure 4.6 and Table 4.1, the Mn concentration increased with the increase of the distance from the surface ($x=0$) until it stabilized at ~27 wt.%. Consequently, this led to a parabolic increase of the partial pressure of Mn as a function of the distance $x$ ($0 < x \leq MDR$) from the surface ($x=0$), as shown in Figure 4.12.

The data in Figure 4.12 shows that the partial pressure of Si in the ternary compacts, regardless of temperature and distance from the surface $(x)$, was much lower than the pressure (~$5 \times 10^{-3}$ Pa) in the furnace during sintering. This completely suppressed the sublimation of Si in the open pores, which agreed with the data in Table 4.1.

Figure 4.12 shows that the vapour pressure of Fe in the ternary alloys decreased with the increase of distance from the surface $x$ ($0 < x \leq MDR$). This reveals that a negative concentration gradient of Fe vapour pressure formed in the open pores of the sintered compacts. According to Fick’s first law, a negative concentration gradient of Fe vapour
prevented the flowing of Fe vapour from the interior area to the vacuum chamber through open pores, and therefore inhibited the sublimation of Fe in the open pores.

By contrast, the concentration of Mn vapour increased gradually with the increase of the distance from the surface ($0 < x \leq MDR$) of the compacts. This promoted the sublimation of Mn as Mn vapour was enabled to flow from the interior area to the vacuum chamber due to the concentration gradient of Mn vapour. Therefore, the weight loss in the internal ($x > 0$) of the compacts is attributed to the sublimation of Mn on the open pore walls.

4.5.2 Effect of open porosities on the weight loss of Mn in Fe-Mn-Si alloys

Figure 4.3 demonstrated that the weight loss of MM alloys is much less than their BE counterparts sintered at the same temperature. The lower weight loss of the MM alloys was caused by the less sublimation of Mn due to the lower open porosities in MM alloys.

Mechanical milling (MM) makes great contribution to pore elimination during sintering as MM effectively refines particle size. This is evidenced by Figure 4.1. Smaller particles provide larger driving force to promote the pore elimination as a result of the higher surface energy of the MM powder mixture [66]. Therefore, the open porosity of MM alloys was significantly lower than their BE counterparts sintered at the same temperature.

As discussed in Section 4.1, the sublimation rate of Mn is predominant over that of Fe and Si. Therefore, we only discuss the sublimation of Mn in this section.

Open pores are regarded as a flow channel to transform the Mn vapour sublimated on the walls of the open pores from the interior area of the compacts to the vacuum chamber.

The BE alloys presented higher open porosities compared to their MM counterparts. This is supported by both Figure 4.9 and the SEM micrographs shown in Figure 4.14. The higher open porosities in the BE alloys offer both larger areas of walls provided by open pores and more flow channels to accelerate the sublimation of Mn in the open pores of the ternary Fe-
Mn-Si compacts. Consequently, the weight loss of Mn was significantly faster in the BE compacts than their MM compacts sintered at the same temperature.

Figure 4.14  SEM micrographs of the Fe-Mn-Si compacts sintered for 3h:  (a) BE alloy at 1100 °C,  (b) BE alloy at 1200 °C, (c) MM alloy at 1100 °C, (d) MM alloy at 1200 °C.

4.5.3 Formation mechanism of MDR region

As shown in Table 4.1 and Figure 4.6, the MDR region exhibited in all the sintered Fe-Mn-Si compacts. Moreover, the length of the MDR region was various depending on sintering temperature and open porosities.

To investigate the effects of sintering temperature and open porosities on the formation of MDR, a model is sketched, as shown in Figure 4.15. It is noted that this model was
established based on the homogeneous distribution of Mn concentration (28 wt.%) in the ternary Fe-Mn-Si compacts.

It is obvious that the sublimation of Mn and the homogenisation of Mn distribution in the Fe-Mn-Si compacts commenced simultaneously during sintering. The EDX results of the samples without isothermal holding (See Figure 4.10) demonstrate that BE compacts at 1100°C and MM compacts at 1000°C gained a relative stable Mn concentration (ranging 24.5% from to 30 wt.%). On the other hand, Figure 4.6 and Table 4.1 show that the MDR of both the BE compacts at 1100°C and MM compacts at 1000°C presented a low MDR value (<10μm). In other words, the sublimation of Mn can be ignored at the stage without isothermal holding compared to that at isothermal holding stage. In this case, we can simplify the sublimation of Mn under the condition that Mn concentration presented a homogeneous distribution.

In the pore-free area of the ternary Fe-Mn-Si compacts, the sublimation of a component only occurs on the surface (x=0) between the gas phase in the vacuum chamber and surface of the compacts directly exposed to the gas phase. The sublimation of Mn on the surface (x=0) resulted in the formation of Mn concentration gradient in Fe-Mn-Si compacts. Consequently, the MDR region formed in the sintered alloys (Curve c in Figure 4.15 (b)).
Figure 4.15 The formation mechanism of MDR in the sintered Fe-Mn-Si alloys as a function of distance (x) from the surface (x=0) at a certain time during isothermal holding. (a) is the cross-sectional sketch of the porous Fe-Mn-Si alloys; (b) shows the change of Mn concentration as a function of distance from the surface of the porous Fe-Mn-Si alloys, curves c and d in (b) show the change of Mn concentration of the sintered Fe-Mn-Si compacts in the pore-free area and open pore area, respectively. C_0 is the Mn concentration on the surface (x=0), C_1 and C_2 is the Mn concentration of the compacts in pore-free area and open pore area at distance x=m, respectively. C_s is initial Mn concentration (~ 28 wt.%) with no sublimation of Mn.
As shown in Figure 4.15, the sublimation rate of Mn on the surface (x=0) of both the BE and MM compacts increased with increase of sintering temperature. Moreover, the rise of sintering temperature remarkably increased the diffusivity of Mn atoms in the Fe-Mn-Si alloys based on Arrhenius’ equation [66]. In other words, the increase of sintering temperature led to more Mn atoms diffusing from the interior region (x>0) to the surface (x=0). Hence, the increase of sintering temperature resulted in an increase of the MDR region in pore-free areas due to the significant increase of Mn sublimation rate on the surface (x=0) and the diffusivity of Mn atoms.

In addition to that, the open pores affect the MDR as well. As discussed in Section 4.2, the open pores significantly accelerated the sublimation of Mn due to the extra area of interface created by walls of open pores. When the distance from the surface is x = m (0<m<MDR) in the sintered alloys, the Mn concentration (curve c in Figure 4.15 (b)) in the Fe-Mn-Si compacts is only determined by temperature-induced sublimation of Mn on the surface (x=0) if no pores existed in the compacts. However, if open pores exist in the compacts, Mn sublimes on the walls of the open pores, and evacuates to the vacuum chamber via the open pores. Consequently, Mn concentration (C2) at position x (x = m, 0<m<MDR) on the interface of the open pores is lower than that (C1) in the pore-free alloys at the same position. Thus, a higher Mn concentration gradient formed in the porous compacts at position x=m compared to the pore-free compacts at the same position. This accelerates the diffusion of Mn atoms at the position x=m. In our case, the BE compacts presented much higher open porosities compared to their MM counterparts. The higher porosities in BE compacts provided more sites to form curve-d shown in Figure 4.15 (b). This accelerates the increase of MDR. Thus, the MDR region in BE alloys is much thicker than their MM counterparts after sintering for 3h at the same temperature.

It is pointed out that the Mn concentration in all sintered compacts stabilized at ~27 wt.% when the distance was ≥MDR. This reveals that the sublimation of Mn in the sintered alloys at distance ≥MDR was very limited as the Mn concentration in the sintered compacts was only ~1 wt.% lower than their designed composition (28 wt.%) in the green compacts. This was caused by a stable Mn partial pressure due to the homogeneous Mn concentration (~27 wt.%) at the distance ≥MDR in the Fe-Mn-Si compacts. The stable equilibrium partial pressure of Mn in the open pores means that no concentration gradient of Mn partial pressure
existed in the open pores. This suppressed the sublimation of Mn at distance $\geq$ MDR in the Fe-Mn-Si compacts. Consequently, the Mn concentration in the positions with distance larger than MDR is stable at $\sim$ 27 wt.%.

### 4.6 Conclusions

This work investigated the effects of sintering temperature and mechanical milling (MM) on the sublimation behaviour of the sintered Fe-28Mn-3Si powder compacts. The key results of this study are summarized below.

1. The phase on the surface ($x=0$) of the sintered compacts is $\alpha$-Fe. The predominant phase for all the sintered alloys was $\gamma$-austenite when the distance from the surface was $\geq$ MDR. A large amount of Mn$_3$Si phase was identified in the sintered BE Fe-Mn-Si compacts.

2. The open porosities of the BE alloys was significantly higher than their MM counterparts. The open porosities of the BE alloys ranged between 33.5% and 29%, while that of the MM alloys reduced remarkably from 25% at 1000°C to 7.6% at 1200 °C.

3. The weight loss of all the sintered compacts was mainly caused by the sublimation of Mn. The weight loss of all the sintered alloys increased significantly with the increase of sintering temperature. The weight loss of the MM alloys was much lower than their BE counterparts.

4. The Mn concentration gradually increased with the increase of the distance from the surface until it stabilized at $\sim$ 27 wt.% when the distance was $\geq$ MDR. The MDR of the sintered alloys depended on a combined consequence of the sintering temperature and characteristic of the powder mixtures. The MDR increased significantly with the increase of sintering temperature. The MDR of the MM alloys was much shorter than their BE counterparts.
Chapter 5 Effects of mechanical milling and sintering temperature on the densification, microstructure and mechanical properties of the Fe-Mn-Si powder compacts

5.1 Introduction

Fe-Mn-Si alloys with a high Mn content (≥ 20 wt.%) have attracted considerable attention over the last few decades due to their unique shape memory effect caused by a reversible phase transformation between the face-centred cubic (fcc) austenitic phase and hexagonal close packed (hcp) martensitic phase [197-201]. One prominent advantage of Fe-Mn-Si shape memory alloys is their low cost [212, 213]. In addition, these high-Mn shape memory alloys exhibit a high flow stress and large elongation and are promising to be developed as TRIP (‘transformation induced plasticity’) and TWIP (‘twinning induced plasticity’) steel [214]. More recently, a ternary Fe-30Mn-6Si alloy was reported to be an attractive candidate for degradable biomaterials due to its high cell viability, low haemolysis, good mechanical properties and good degradation rate [38, 202].

Published work on Fe-Mn-Si alloys mainly focuses on civil applications such as pipe joints and dampers [213, 215, 216]. Research on their biomedical applications emerged only recently. The mainstream manufacturing method for Fe-Mn-Si alloys is via the traditional casting and wrought route. An alternative manufacturing technique – powder metallurgy (PM) – has its own unique advantages. As a net-shaping or near net-shaping technique, PM significantly reduces the secondary machining operations and decreases the amount of the waste materials generated [65, 217].

Over the past decades, P/M Mn ferrous alloys and steels have been extensively investigated, particularly in the context of the revisited interest in high-strength steels. In this regard, PM technologies offer some advantages over ingot metallurgy. One issue associated with PM high-Mn alloys is the sublimation of Mn element [218, 219]. The majority of investigations focused on compositions with low Mn concentration (<5 wt.%) [220].
Mechanical milling (MM) is a well-established powder production technique. In some cases, MM can be used to synthesise non-equilibrium alloys. In addition to its ability of refining powder particle size, MM is able to generate a refined layered microstructure if the powder mixture contains two or more powders. The much refined particle size and refined microstructure are beneficial to promote the powder densification as the diffusion path is significantly shortened. As a result, sintering can be performed at a lower temperature and with a shorter sintering time [66]. For the same reasons, the issue of Mn sublimation would be minimised by mechanical milling. It is therefore important to investigate how mechanical milling affects the resulting microstructure and mechanical properties of the sintered Fe-Mn-Si alloys that contain high Mn contents.

5.2 Experimental

5.2.1 Materials

Commercially available pure elemental Fe, Mn and Si powders were used as the starting materials. The morphologies of these starting powders are shown in Figure 3.2. All these starting powders were of angular shape. Table 3.4 summarises the impurity level and particle size distribution. Two batches of powder mixture were prepared. The first batch was a blended elemental (BE) powder mixture without mechanical milling, where the elemental Fe, Mn and Si powders were simply blended for 10 h with a nominal composition of 69%Fe, 28% Mn and 3% Si (all in weight percent). The second batch was prepared by mixing and subsequent mechanical milling (MM). Detailed information on the MM parameters was shown in Chapter 4.

5.2.2 Press and sinter

Both BE and MM powder mixtures were then pressed into rectangular samples with dimensions of 40 mm x 16 mm x 4.2 mm, under a pressure of 400 MPa at room temperature. Subsequently, all these green compacts were sintered in a high vacuum furnace at 5x10⁻³ Pa. The temperature profile during sintering is shown in Figure 5.1. It is noted that the different heating rate set-up below and above 800 °C were required as per the furnace specifications. Both BE and MM compacts were sintered for 3 h at 1000, 1100, 1200 and 1300 °C,
respectively, followed by furnace cooling. Macroscopic images of the green compacts and the sintered alloys are shown in Figure 5.2, which clearly shows swelling occurred in the compacts sintered at 1000 °C.

Figure 5.1  Heating profile of Fe-28Mn-3Si powder mixture sintered for 3h at different sintering temperatures.

5.2.3 Characterization

Density and porosity of all the sintered compacts were measured by Archimedes’ principle as specified in the ASTM B962-13 standard. Theoretical density of a fully dense Fe-28wt.%Mn-3wt.%Si sample is 7.50 g/cm³[202]. The sintered density of the sintered PM alloys is then calculated by $D = \frac{\rho_1}{\rho_0}$ and expressed in %TD (percentage of theoretical density), where $\rho_0$ is the theoretical density (g/cm³) of the pore-free Fe-28wt.%Mn-3wt.%Si alloy as specified above, $\rho_1$ is the measured density of the sintered Fe-28wt.%Mn-3wt.%Si samples.
5.3 Results

5.3.1 Chemical composition

Figure 5.3 shows the Mn concentration as a function of the distance measured from the surface on the cross-section of the sintered compacts. The EDX results in Figure 5.3 reveal that a Mn depletion region (MDR) existed in all the sintered compacts due to the sublimation of Mn during sintering. However, the Mn concentration levelled off to ~ 28 wt.% -- the designed Mn concentration, at a distance beyond MDR. Table 5.1 summarises the data of MDR thickness, chemical compositions beyond MDR in both BE and MM compacts sintered at various temperatures. Concurrent with the swelling (Figure 5.2) in the compacts sintered at 1000 °C, the compositions in these compacts varied significantly (Mn from 10.5 to 38.7%). In other words, the sintering temperature of 1000 °C did not lead to a homogeneous elemental distribution in the powder compacts. If the temperature was further increased above 1100 °C, the compositional homogenisation was achieved after sintering. It is noteworthy that the thickness of MDR largely depended on the sintering temperature; a higher sintering temperature resulted in a thicker MDR, indicating a higher sublimation rate at a higher temperature. If the temperature was excessively high, e.g. at 1300 °C, the Mn loss was observed in the entire BE compacts – a significantly lower Mn content < 5.3% throughout the entire thickness of the cross section (Figure 5.3b). In remarkable contrast, the thickness of MDR in the MM compacts was much less than that of the BE compacts. Even at 1300 °C, the MM compact had an MDR thinner than the BE compacts at 1100 °C. In the subsequent analyses and characterisation, the scale of MDR was removed from the sintered compacts, except for the BE compacts sintered at 1300 °C.
Figure 5.2 Macroscopic images of Fe-Mn-Si alloys after being sintered for 3 h at different temperatures: (a) BE compacts and (b) MM compacts.

Figure 5.3 Mn concentration at the cross-section of the sintered Fe-Mn-Si alloys at different temperatures for 3h: (a) BE compacts sintered at 1200 °C, (b) BE compacts sintered at 1300 °C, (c) MM compacts sintered at 1300 °C.
Table 5.1 Thickness of MDR and the average chemical compositions of the sintered Fe-28Mn-3Si compacts

<table>
<thead>
<tr>
<th>Type of powder mixture</th>
<th>Sintering temperature</th>
<th>The thickness of MDR (μm)</th>
<th>Chemical composition (wt.%)&lt;sup&gt;△&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn</td>
</tr>
<tr>
<td>BE</td>
<td>1000</td>
<td>-&lt;sup&gt;☆&lt;/sup&gt;</td>
<td>10.5~38.7*&lt;sup&gt; *&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>650 ±35</td>
<td>25.3 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>1250 ±56</td>
<td>27.9 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>-&lt;sup&gt;☆&lt;/sup&gt;</td>
<td>5.1*</td>
</tr>
<tr>
<td>MM</td>
<td>1000</td>
<td>-&lt;sup&gt;☆&lt;/sup&gt;</td>
<td>14.8 ~ 30.2*&lt;sup&gt; *&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>255±23</td>
<td>27.9 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>500±31</td>
<td>27.5 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>550±45</td>
<td>26.8 ± 1.3</td>
</tr>
</tbody>
</table>

<sup>△</sup> The chemical compositions of both the BE and MM compacts were measured by EDS. It is noted that the chemical compositions of all the sintered compacts in this paper refer to the chemical compositions at the distance from the surface ≥ MDR if there is no special specification.

* For both BE and MM compacts sintered at 1000°C, the chemical compositions fluctuated due to incomplete sintering. For the BE compacts sintered at 1300°C, Mn content was significantly low (2.5% measured on the surface and 7.5% measured in the middle of the cross-section). This is caused by severe Mn sublimation.

# The thickness of MDR was not measured due to the fluctuation of the Mn content in the compacts sintered at 1000 °C.

☆ Severe Mn depletion occurred in the entire BE compacts sintered at 1300 °C.
5.3.2 Sintered density

Figure 5.4 shows the relative density of the BE and MM Fe-28Mn-3Si compacts as a function of sintering temperature. The sintered densities of the MM compacts increased sharply with sintering temperature. For instance, the MM compacts sintered at 1300°C presented a density of ~ 91%TD, as compared with 65%TD of the compact sintered at 1000 °C. In contrast, the BE compacts sintered at all temperatures had a relatively low density ranging from ~63%TD to 68.2%TD. The green density of both BE and MM green compacts is included in Figure 5.4 for comparison purpose. The green density of the BE compacts was approximately 68.5wt.%, 3wt.% higher than their MM counterparts. Considering the higher green densities in BE compacts, the densification level of the MM compacts was much higher than the BE compacts. In other words, mechanical milling has significantly enhanced the subsequent sintering densification.

Figure 5.4  Sintered density of BE and MM compacts sintered for 3 h as a function of sintering temperature, and the relative density of BE and MM green compacts at room temperature (Note: The relative density of the BE alloys sintered at 1300 °C is not given, due to significant sublimation of Mn during sintering at this temperature, as shown in Table 5.1).
5.3.3 Microstructural evolution

Figure 5.5 illustrates the SEM micrographs of both BE and MM green compacts. It can be seen that after mechanical milling the particle size of both Mn and Si powders had reduced significantly to < 6μm, while Fe powder particles were elongated. This is expected because Mn and Si are brittle while Fe is ductile. Figure 5.6 shows the microstructures of the sintered BE compacts at various sintering temperatures. A large number of angular and irregular pores with sizes ranging from 50μm to 100 μm were visible in the compacts sintered at 1000 °C and 1100 °C. Furthermore, most of the pores were interconnected, indicating that the sintering was incomplete at ≤ 1100 °C. Many large round grey particles (e.g., square box A in Figure 5.6) were observed. The EDX results indicated that these grey particles were Si-rich, suggesting that the large Si particles in the green compacts did not diffuse into γ-austenite phase during sintering at 1000 °C. According to the isothermal section of the ternary Fe-Mn-Si phase diagram at 1000°C [221] and EDX results, these grey particles in the BE compacts sintered at 1000 °C are intermetallic Mn₃Si phase. If the compact was sintered at 1100 °C or 1200 °C, the major phase was γ-austenite in the absence of intermetallic Mn₃Si, as shown in Figs. 5.6 (b) and (c). It is noted that the BE compacts sintered at 1300 °C revealed much larger-sized pores, accompanied with the significantly different compositions (determined by EDX measurements, see Table 5.1 for details).
Figure 5.5 Microstructure of Fe-Mn-Si green compacts: (a) BE green compacts, (b) MM compacts, (c) enlarged rectangular area in (b).
Figure 5.6 SEM micrographs of BE compacts sintered at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) EDX spectrum from the square box ‘A’ in (a).
Figure 5.7 shows the SEM micrographs of the MM compacts sintered at different temperatures. As seen in Figure 5.7 (a), the sintering of the MM compacts at 1000 °C was incomplete, evidenced by a large number of interconnected and irregular pores. This is similar to the morphology of the BE compacts sintered at the same temperature. However, it is noted that no secondary phase or Si-rich phase were observed in Figure 5.7 (a), suggesting that both Si and Mn particles have completely diffused into γ-austenite matrix when the compact was sintered at 1000 °C. When the sintering temperature was increased to 1100 °C, the pore size reduced, although the pores were still angular and elongated. A further increase in sintering temperature to 1200 °C and 1300 °C led to a significant reduction in pore size and pore population. The residual pores were isolated and smooth (arrow C in Figure 5.7 (c)), a typical indication of the final sintering stage. The EDX result confirmed that the black particles are Mn- and Si-rich oxides.
5.3.4 Phase identification

Figure 5.8 presents the XRD results of both the BE and 5h MM green compacts. As shown in Figure 5.8, both the BE and MM green compacts exhibited the same phase constituents. This demonstrates that 5 h milling did not cause mechanical alloying. Figure 5.9 and Figure 5.10 present the phase constituents of both BE and MM compacts sintered at different temperatures. In the case of the BE compacts, predominant γ-austenite phase and minor ε-martensite phase were identified in the compacts sintered at <1200 °C. In addition, peaks indexed to intermetallic Mn₃Si were observed in the BE compacts sintered at 1000 °C only. No peaks corresponding to Mn₃Si phase were identified in the BE compacts sintered at 1100 °C.
and 1200 °C. However, α-Fe ferrite was the only phase observed in compacts sintered at 1300 °C. In the case of the MM compacts, γ-austenite is the dominant phase in all the compacts (See Figure 5.10) regardless of sintering temperature. A minor ε-martensite phase was identified in all these MM sintered compacts.

Figure 5.8  XRD patterns of the BE green compacts (a) and 5h MM green compacts (b).
Figure 5.9  XRD patterns of the BE compacts sintered for 3h at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C.

Figure 5.10  XRD patterns of the MM compacts sintered for 3h at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C.
5.3.5 Static tensile testing

Engineering stress-strain curves of the best quality Fe-28Mn-3Si compacts sintered from BE or MM powder mixtures are shown in Figure 5.11. Both curves illustrate characteristic strain hardening. The ultimate tensile strength (UTS), fracture strain ($\varepsilon$) and Young’s modulus ($E$) of all the sintered compacts are summarised in Table 5.2. In general, the UTS, $\varepsilon$ and $E$ increased with increasing sintering temperature for both BE and MM compacts. A comparison of the BE compacts with MM compacts indicates that the mechanical properties of the compacts sintered from BE compacts were relatively low and the elevated sintering temperature only resulted in a limited improvement in mechanical properties. The highest values for UTS (155 MPa), $\varepsilon$ (3.3%) and $E$ (30.3 GPa) among all the BE compacts were observed in the compact sintered at 1300 ℃. In contrast, the mechanical properties of the MM sintered compacts are significantly higher, largely due to the higher densification attained in the MM compacts. Sintering temperature seems to have a prominent effect on the mechanical properties of these MM sintered compacts. The UTS and $E$ values of the MM compacts sintered at 1300 ℃ were 454.5 MPa and 102 GPa, 190% and 240% higher than the BE compacts sintered under the same conditions.

Figure 5.11 Tensile stress-strain curves of Fe-28Mn-3Si compacts sintered at various sintering temperatures: (a) BE compact at 1300 ℃, (b) MM compact at 1300 ℃.
Table 5.2  Static tensile properties of Fe-Mn-Si alloys sintered for 3h at different sintering temperatures.

<table>
<thead>
<tr>
<th>Type of sintered powder mixture</th>
<th>Sintering temperature/°C</th>
<th>Ultimate tensile strength/MPa</th>
<th>Fracture strain/%</th>
<th>Young’s modulus/GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blended elemental (BE)</td>
<td>1000</td>
<td>47.6 ± 4.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>84.1 ± 4.2</td>
<td>1.75 ± 0.45</td>
<td>19.8 ± 0.63</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>114.2 ± 9.8</td>
<td>2.66 ± 0.52</td>
<td>30.43 ± 1.74</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>154.9 ± 12.6</td>
<td>3.26 ± 0.63</td>
<td>30.28 ± 0.97</td>
</tr>
<tr>
<td>Mechanical Milled (MM)</td>
<td>1000</td>
<td>89.5 ± 5.2</td>
<td>1.08 ± 0.23</td>
<td>45 ± 2.61</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>214.5 ± 12.1</td>
<td>5.1 ± 0.81</td>
<td>62.14 ± 1.82</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>328.2 ± 27.3</td>
<td>8.45 ± 1.33</td>
<td>79.45 ± 2.69</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>454.5 ± 30.2</td>
<td>11.86 ± 1.12</td>
<td>102.62 ± 4.31</td>
</tr>
</tbody>
</table>

5.4 Discussion

5.4.1 Phase evolution

As shown in Figure 5.6 (a) and Figure 5.9, the Mn₃Si phase was formed in the BE compacts sintered at 1000 °C, but not in the MM compacts sintered at the same temperature. This is because MM had significantly reduced the particle size. MM had also refined the microstructure of the milled powder. In a typical mechanically milled microstructure of a powder mixture of A and B where A is a ductile metal while B is a brittle metal, the particle size of brittle B is reduced and powder B fine particles are often embedded in much deformed powder A, forming a lamellar microstructure [69]. Such a refined microstructure can significantly accelerate the densification process via sintering because the diffusion distance has been much shortened. In the BE compacts (Figure 5.5 (a)), Si particles were surrounded by Mn particles. At 1000 °C, they reacted to form Mn₃Si. In the MM compacts Figure 5.5 (b)
and 5.5 (c) reveals that the particle size of Fe, Mn and Si was much smaller and the mixing of Fe, Mn and Si was more homogeneous. The homogeneous mixing leads to a single γ-austenite phase. The existence of high Si-containing γ-austenite in the BE compacts sintered at 1100 °C is again a consequence of inhomogeneous mixing. Such an inhomogeneous mixing can be remedied by a higher sintering temperature. However, an excessively high temperature would cause serious sublimation (or evaporation) of Mn. The EDS analysis shows that the bulk Mn concentration in the 1300 °C sintered compact was ~ 5 wt.% Mn (Table 5.1). According to the Fe-Mn-Si ternary phase diagram [221], this composition corresponds to a single α-Fe phase.

It is noted that a small amount of ε-martensite phase was generated in the BE compacts sintered at ≤1200 °C and in the MM compacts at all sintering temperatures. The formation of this minor ε-martensite phase in these alloys may occur during furnace cooling after sintering. Figure 5.12 illustrates the effect of Mn and Si content as well as Neel temperature (T_N) on the martensite start temperature (M_s) [222]. As shown in Figure 5.12, in our case, the M_s temperature of all the sintered alloys was higher than room temperature and T_N, indicating that phase transformation from parent γ-austenite phase to ε-martensite phase could be induced in all the as-sintered alloys during furnace cooling. Therefore, it is suggested that the formation of minor ε-martensite phase in the as-sintered alloys was caused by furnace cooling.
5.4.2 Densification

The effect of sintering temperature on densification is predicted by the Arrhenius equation [66]. Based on the available literature data [223-225], diffusion coefficients of Fe, Mn and Si in the γ-austenite phase calculated as a function of temperature are shown in Figure 5.13.
Figure 5.13 demonstrates that the diffusion coefficient of both Mn and Si in γ-Fe increases significantly with sintering temperature. For example, the diffusion coefficient of Mn and Si at 1200 °C increased by approximately 22 and 33 times, respectively, compared to that at 1000°C. Thus, the porosity and pore size of MM alloys decrease significantly when the sintering temperature increases, concomitant with a remarkable increase in densification.

In addition, mechanical milling (MM) affects densification of powder samples, as shown in Figure 5.4. MM causes particle size refinement. It is known that a small particle size corresponds to a large driving force for densification due to the increased surface energy [66]. The particle size refinement has been evidenced and shown in Figure 5.5 and Table 3.4. In addition to refining powder particles, MM is able to generate a composite microstructure containing small Mn or Si within Fe. This refined composite microstructure reduces the diffusion path between the particles during sintering, thereby accelerating densification.
However, it is noted that the density of all sintered BE alloys is relatively low (<68.2%), and no obvious densification happened in the BE alloys. For example, the porosity in the sintered BE alloys at 1000 °C was ~5% higher than their green compacts.

The low densification for the BE alloys may be caused by the alloying process. As shown in Figure 5.13, the diffusion coefficient of Si atoms is more than one order of magnitude higher than Fe and Mn atoms. In addition to that, the binary Fe-Si and Mn-Si phase diagrams [226] reveal that the solubility of both Fe and Mn in Si is close to 0 at temperatures ≤1200 °C. Conversely, the solid solubility of Si in both Fe and Mn is extensive, up to approximately 10 wt.% at > 1000 °C. As a consequence, large pores may be left behind at the sites previously occupied by the Si particles after Si atoms completely diffuse into Fe or Mn particles. Similarly, according to the binary Fe-Mn phase diagram [227], the solubility of Mn atoms in Fe is more than 70 wt.% at 1000 °C, which is again much higher than that of Fe in Mn (less than 30 wt.%) at the same temperature. Pores may be generated when Mn atoms diffuse into Fe matrix. These pores in the BE alloys are difficult to shrink at low temperatures (≤ 1100 °C). Consequently, the porosity of the BE compacts sintered at 1000 °C and 1100°C is almost 5 % and 3.5% higher than their green compact counterparts.

It is noted that the Mn sublimation in the pores of both BE and MM alloys, especially in isolated pores, plays an important role in densification of the sintered alloys. Densification is a process of pore elimination. Published work reveals that the pore elimination depends on a balance between the surface energy in the curved surface of the pores and the gas pressure in the pores [66]. For example, the pore shrinkage stops if the gas pressure trapped in the pores is larger than the surface energy on the surface of the pores. In our case, as shown in Figure 4.12, the equilibrium partial pressure of the component Mn in the ternary Fe-Mn-Si alloys was as high as 16.6 Pa. In other words, the pressure in the pores kept ~16.6 Pa during isothermal holding. This inhibited the pore shrinkage, especially for the isolated pores, and consequently prevents the densification of the sintered compacts.
5.4.3 Tensile properties

The relationship between mechanical properties and porosity was proposed by Gibson and Ashby [228]:

\[
\frac{\sigma}{\sigma_0} = C_1 \left( \frac{\rho}{\rho_0} \right)^{n_1} \quad (5.1)
\]

\[
\frac{E}{E_0} = C_2 \left( \frac{\rho}{\rho_0} \right)^{n_2} \quad (5.2)
\]

where \(\sigma\) and \(E\) are the tensile strength and modulus of elasticity of the sintered alloy, \(\rho\) the density, subscript ‘0’ indicates the pore-free alloy. \((1-\rho/\rho_0)\) is the porosity, \(C_1, C_2, n_1\) and \(n_2\) are material constants depending on the pore structure. As show in the Gibson-Ashby model, the strength and modulus of elasticity increase with the decrease of porosities. This is because a lower porosity gives rise to a higher effective load-bearing cross-sectional area, and therefore leads to higher mechanical strength. Porosity decreases with increasing sintering temperature (Figure 5.4) and therefore tensile strength increases. For the same reason, the MM alloys have a higher strength than the BE alloys when they were sintered at the same temperature.

Figure 5.14 and Figure 5.15 show the microscopic fractography of both BE and MM alloys sintered at different temperatures. As illustrated in Figure 5.14, all sintered BE compacts exhibit a typical brittle failure. Powder detachment is the main rupture mechanism as a result of the weak particle bonding due to the incomplete sintering. However, some cleavage facets and river patterns are visible on the fracture surface of BE compacts when sintering at between 1200 °C and 1300°C. For all MM alloys, a mix of brittle and ductile failure features can be found on the fractured surface. Shallow dimples indicate that ductile fracture occurred in some regions of the MM alloys. Moreover, the dimple feature becomes more prominent in the samples sintered at high temperatures.
Figure 5.14 Fracture surfaces of the Fe-28Mn-3Si alloys sintered from BE powder at different temperatures. (a) 1200 °C, (b) enlarged square area in (a), (c) 1300°C, (d) enlarged square area in (c).
Figure 5.15 Fracture surfaces of the as-sintered Fe-28Mn-3Si alloys sintered from MM powder at different temperatures: (a) 1100 °C, (b) 1200°C, (c) enlarged square area in (b), (d) 1300°C.

5.5 Summary

The effects of mechanical milling and sintering temperature on the microstructure evolution, densification mechanism as well as mechanical properties of the sintered Fe-28Mn-3Si powder compacts were studied. The key findings of this study are summarized below:
(1) Both the sintered blended elemental (BE) and mechanically milled (MM) samples exhibited a Mn depletion region (MDR) layer on the surface. The thickness of the MDR layer increased with the increase of sintering temperature. The MDR thickness of the sintered BE compacts was significantly greater than their MM counterparts at the same sintering temperature.

(2) The BE alloys presented low sintered densities (< 68.2%) at all sintering temperatures, and no densification occurred in the BE alloys. Predominant $\gamma$-austenite phase and minor $\varepsilon$-martensite phase were identified if the sintering temperature was <1200 °C. In addition, a large amount of Mn$_3$Si intermetallic phase formed in the BE alloys sintered at 1000 °C. However, only a single $\alpha$-Fe phase was found in the BE compacts sintered at 1300 °C. When sintering temperature was $\geq$ 1200 °C, a large number of pores with size ~150µm were formed.

(3) The density of the MM alloys increased drastically with the increase of sintering temperature (from ~67% at 1000 °C to ~91% at 1300 °C). The density of the MM alloys was considerably higher than their BE counterparts. The MM alloys were comprised of predominant $\gamma$-austenite and minor $\varepsilon$-martensite at all sintering temperatures. The pore size of MM alloys decreased significantly with the increase of sintering temperature.

(4) The mechanical properties are determined as a combined consequence of starting particle size and sintering temperature. In general, the mechanical properties of both BE and MM alloys increased with increasing sintering temperature. The strength and ductility of MM alloys, were remarkably higher than their BE counterparts.
Chapter 6 Effect of sintering time on the densification, microstructure and mechanical properties of a PM Fe-Mn-Si alloy

6.1 Introduction

In the past, few published works have discussed the powder preparation and the sintering behaviours of Fe-Mn-Si alloys [87, 88, 229]. In this chapter, we investigated the effect of isothermal time on the microstructure and mechanical properties of the sintered MM Fe-28wt.%Mn-3wt.%Si. Reasonable holding time is necessary to obtain Fe-Mn-Si alloys with optimal microstructure and mechanical properties. Therefore, we aim to explore the evolution of the microstructure and mechanical properties of the sintered Fe-Mn-Si alloys as a function of isothermal holding time.

6.2 Experiment

6.2.1 Powder preparation

Three elemental powders were selected as the starting materials in this study: Fe (99.9% purity), Mn (99.7% purity) and Si (99.95% purity). XRD patterns (Figure 3.3) reveal that all powders presented a single phase. The mean particle sizes of Fe, Mn and Si powders are 38.6, 38.7 and 43.4μm, respectively. The morphologies of these particles are shown in Figure 3.2, where all these three powders exhibit an angular shape.

Powder mixtures with a nominal composition of 69 wt.% Fe, 28 wt.% Mn and 3 wt.% Si were used in our study. All powder mixtures were formed with mechanical milling (MM) for 5h. Detailed information on the MM parameters is shown in Chapter 4.

6.2.2 Press and sinter

MM powder mixtures were then compacted in a rectangular die under a pressure of 400 MPa at ambient temperature. The green compacts were subsequently sintered in a high vacuum
furnace of $5 \times 10^{-3}$ Pa. The heating ramp was $10^\circ$C/min below $800^\circ$C and $5^\circ$C/min above $800^\circ$C. All samples were sintered at $1200^\circ$C with a wide range of isothermal holding times from 0 to 3h, as shown in Figure 6.1. It is noted that the selection of $1200^\circ$C is based on optimal results in Chapter 4 and 5 regarding the sublimation of Mn, densification, and energy consumption.

![Figure 6.1 Heating profile of the Fe-28Mn-3Si powder mixture sintered at 1200°C for different isothermal time.](image)

**6.3 Results**

**6.3.1 Density and porosity**

Figure 6.2 shows the dependence of the relative density and open porosity of the Fe-28Mn-3Si alloys sintered at $1200^\circ$C, upon sintering time (The error bar here sintered at $1200^\circ$C for 3 h is slightly different from that in Fig. 5.1 sintered at the same condition. The slight change to the deviation of the sintered density may be caused by combined consequences of mechanical milling, powder compaction, sintering and density test. The density from these two figures are measured based on two different batches of samples. In other words, the error
bar in each figure was calculated based on the corresponding specific batch of samples). It is noted that a drastic increase in relative density occurred in alloys sintered for 1h. In detail, the relative density of alloys sintered for 1 h was approximately 80%, an increase of ~11% compared to alloys (69%) with no holding time. Interestingly, longer sintering time did not lead to a significant increase in density when isothermal holding time was >1h. For example, the density in alloys sintered for 3 h was ~84.5%, which is only increased by ~4% and ~1% with respect to their counterparts sintered for 1h and 2h, respectively.

In general, the open porosities of all the sintered alloys decreased with the increase of sintering time. The open porosity in alloys sintered with no isothermal holding was around 25%, and it sharply reduced to 11.9% after 1h isothermal holding. However, further increase in isothermal time only had a limited effect on decreasing open porosities.

![Figure 6.2](image.png)

Figure 6.2 Relative density and open porosities of the Fe-Mn-Si compacts sintered at 1200°C as a function of isothermal holding time.
Figure 6.3 Morphologies of the MM Fe-Mn-Si compacts sintered at 1200°C for various isothermal time: (a) 0h, (b) 1h, (c) 2h, (d) 3h.

Figure 6.3 shows the SEM graphs of Fe-28Mn-3Si alloys sintered at 1200°C as a function of isothermal time. Figure 6.3 (a) illustrated that a large number of interconnected irregular pores were distributed in the alloys with no isothermal holding, indicating that sintering at this stage was incomplete. When isothermal time increased to 1h, the pore size as well as the overall porosities, especially interconnected pores reduced to a large extent. However, most of the pores still exhibited irregular shape. As the time increased to 2h, the pore size further decreased, and part of the pores became spherical and isolated. It is noted that the morphology of the alloys sintered for 3h was similar to that for 2h. However, more isolated and spherical pores were observed in compacts sintered for 3h, as shown in Figure 6.3 (d).
6.3.3 Weight loss and composition change

Figure 6.4 Weight loss rate of the sintered MM Fe-Mn-Si samples as a function of isothermal time.

Figure 6.4 shows the weight loss of the alloys sintered for different isothermal times. In general, the weight loss rate increased with the increase of isothermal time. In detail, the weight loss rate of the sintered MM alloys without isothermal holding was very limited, only ~2wt.% When the isothermal time increased to 1h, the weight loss increased significantly to ~7.4 wt.%, which is more than 3-fold that of their counterparts without isothermal holding. However, the weight loss rate of the alloys sintered for 2h and 3h increased by only 2.1wt.% and 3.4 wt.% compared to that sintered for 1h. This indicates that the weight loss mainly occurred in the first hour of isothermal holding.

An EDS line scan was performed on the cross sections of the sintered compacts to examine the composition. As shown in Figure 6.5, the EDS line scan direction was perpendicular to sample-resin interface, and all scans recorded from the interface to the middle regions of the
cross sections. Table 6.1 and Figure 6.6 provide comprehensive details on the composition of the sintered alloys. The surface of all the sintered alloys presented a low Mn content (< 1.5wt.%). The Mn content increased parabolically with the increase of distance from the resin-sample interface of all the sintered samples until it stabilized at ~27 wt.%. By contrast, the Si content was ~ 3.2 wt.% at all distance. We define the scan distance between the resin-sample interface (x=0) of the sintered samples and the position that Mn content reached a stable value (~27wt.%) as the length of unstable Mn distribution region (MDR). Interestingly, the MDR increased with the increase of isothermal time, as shown in Table 6.1.

Figure 6.5 The morphlogies of the cross-section of the MM Fe-28Mn-3Si alloys sintered at 1200°C for 1h.
Table 6.1  The chemical composition of the MM ternary Fe-Mn-Si alloys sintered at 1200 °C for different isothermal time.

<table>
<thead>
<tr>
<th>Isothermal time</th>
<th>Chemical composition on the surface (wt.%)</th>
<th>MDR (μm)</th>
<th>Chemical composition (wt.%) at positions ≥MDR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>Si</td>
<td>Fe</td>
</tr>
<tr>
<td>0</td>
<td>&lt;3.21</td>
<td>Bal.</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>&lt;3.36</td>
<td>Bal.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>&lt;3.25</td>
<td>Bal.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>&lt;3.07</td>
<td>Bal.</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.6  Mn and Si concentration in the cross section of the MM Fe-Mn-Si alloys sintered at 1200°C for 1h.
6.3.4 Phase identification

Figure 6.7 XRD results on the surface of the ternary Fe-28Mn-3Si alloys sintered at 1200°C for different isothermal holding time. (a) MM alloys without isothermal holding, (b) MM alloys for 1h isothermal holding, (c) MM alloys for 2h isothermal holding, (d) MM alloys for 3h isothermal holding.
Figure 6.8  XRD results on middle parts (≥ MDR region) of the ternary Fe-28Mn-3Si alloys sintered at 1200°C for different isothermal time. (a) MM green compacts before sintering, (b) MM alloys without isothermal holding, (c) MM alloys for 1h isothermal holding, (d) MM alloys for 2h isothermal holding, (e) MM alloys for 3h isothermal holding.

Figure 6.7 and Figure 6.8 show the XRD results of the ternary alloys on the surface and middle part, respectively. Figure 6.8 (b) illustrates that no peaks belonging to Fe, Mn or Si were observed in the sintered alloys. This indicates that both Mn and Si dissolved in the Fe matrix during the ramp stage. Figure 6.8 also reveals that all sintered alloys comprised of a duplex major γ-austenite and minor ε-martensitic phase. Figure 6.7 shows that the surface of all sintered alloys presented only a single α-Fe phase, regardless of the isothermal time.
6.3.5 Mechanical properties

Figure 6.9  Tensile stress-strain curves of MM Fe-28Mn-3Si compacts sintered at 1200°C for various isothermal time: (a) 1h, (b) 2h, and (c) 3h.

Table 6.2  Static tensile properties of the Fe-Mn-Si alloys sintered at 1200°C for different isothermal time.

<table>
<thead>
<tr>
<th>Sintering temperature/°C</th>
<th>Holding time/h</th>
<th>Ultimate tensile strength/MPa</th>
<th>Fracture strain/%</th>
<th>Young’s modulus/GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>1</td>
<td>257.9 ± 8.9</td>
<td>6.43 ± 0.52</td>
<td>69.14 ± 2.55</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300.1 ± 15.2</td>
<td>7.6 ± 0.61</td>
<td>71.38 ± 2.72</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>337.2 ± 23.3</td>
<td>9.2 ± 0.56</td>
<td>73.52 ± 3.21</td>
</tr>
</tbody>
</table>

Figure 6.9 and table 6.2 illustrate the stress-strain curves and the mechanical properties of the sintered alloys with different isothermal time. In general, the mechanical properties of the sintered compacts increased gradually with the increase of isothermal time. For example, the
UTS and fracture strain of the alloys sintered for 2 h is 300 MPa and 7.6%, which is ~70 MPa and 1.2% higher than their counterparts sintered for 1h.

6.4 Discussion

6.4.1 Weight loss

Figure 6.10  Mn and Si concentration in the cross section of MM Fe-Mn-Si alloys sintered at 1200°C with no isothermal holding.

Figure 6.10 shows Fe, Mn and Si homogenously distributed in the sintered ternary compacts without isothermal holding, in which the concentration of Fe, Mn and Si stabilized at ~ 69 wt.%, 28 wt.% and 3 wt.% at all distances. This composition belongs to γ-austenite according to the XRD result and the SEM micrographs, as shown in Figure 6.3 (a) and Figure 6.8 (b). As discussed above, all the Fe-Mn-Si compacts are in solid state (γ-austenite) during isothermal holding so it is therefore believed that the weight loss of the ternary Fe-Mn-Si compacts is attributed to the sublimation of the components (Fe, Mn and Si) during sintering.
As discussed in Section 4.4.1 of Chapter 4, the weight loss of the binary Fe-Mn-Si system is attributed to the sublimation of Mn during sintering at 1200°C.

Open pores play an essential role in the weight loss of the compacts during sintering. This is because open pores create a large amount of walls, which are sites for the sublimation of Mn. Moreover, open pores are regarded as flow channels to transport the Mn vapour from the internal area to vacuum chamber in porous materials.

It is noted that the weight loss of the sintered compacts isothermally held in the second and third hours was 1.7 wt.% and 1.15 wt.%, respectively, which is only ~ 1/3 and 1/5 of that in the first hour of isothermal holding. This demonstrates that the sublimation rate of Mn decreases with the increase of isothermal time. This is caused by a decrease in open porosities due to a longer isothermal holding.

The increase of isothermal time led to a decrease in open porosities, as demonstrated in Figure 6.2. Higher open pores presented higher Mn sublimation due to higher wall areas of open pores and more flow channels for transferring Mn vapour. In our case, the open porosities in compacts sintered at the beginning of isothermal holding was ~ 24.9%, and it significantly decreased to ~11.9%, 9.2% and 7.67% after 1h, 2h and 3h isothermal holding, respectively. Therefore, the remarkably higher open pores during isothermal holding in the first hour gave rise to a significantly higher weight loss compared to those sintered in the second and third hours.

6.4.2 Densification

It is recognised that the elimination of surface energy is the driving force for powder densification [66]. The density of the sintered alloys with no holding was ~ 5% higher than their green compacts. This demonstrates that densification happened in compacts with no isothermal holding. The densification of the samples sintered at the stage without isothermal holding may be mainly attributed to the release of the stored surface energy in the MM starting powders.
The XRD result shows that a single $\gamma$-austenite phase was formed and no peaks belonging to $\alpha$-Fe, Mn and Si were detected in powder compacts with no isothermal holding. This reveals that alloying was completed in the temperature-rising stage. Therefore, it is believed that the densification in the temperature-rising stage was mainly caused by the released surface energy of the MM elemental powders during alloying.

Interestingly, a rapid densification of the Fe-Mn-Si compacts occurred in the first hour of isothermal holding. Figure 6.2 shows that the density of the compacts after 1h isothermal holding increased by 11% compared to that with no isothermal holding. As discussed above, alloying completed before the start of isothermal holding; therefore, the rapid densification of compacts in the first hour of isothermal holding may be driven by the diminution in the surface energy due to the reduction in the volume and the surface areas of the pores.

However, further increase of isothermal holding ($\geq$ 1h) has a limited promotion in densification, e.g., the density of the alloys holding for 2h and 3h is $\sim$ 83% and $\sim$ 84.5%, which is only 3% and 4.5% higher than their counterparts holding for 1h. This may be attributed to the following factors. Firstly, the remarkable decrease in open porosities contributed to the slow densification of the compacts when the isothermal holding time $\geq$ 1h. Figure 6.2 shows that open porosities of the compacts sintered for 1h isothermal holding are only 1/2 of the compacts sintered with no isothermal holding. The serious decrease in open porosities of the compacts sintered for longer than 1h resulted in a severe reduction in surface area. Consequently, the density of the alloys holding for $\geq$ 1h increased slowly with the increase of isothermal holding time. In addition to that, the Mn sublimation in the pores, especially in isolated pores, plays an important role in densification of the sintered alloys. Densification is a process of pore elimination. Published work reveals that the pore elimination depends on a balance between the surface energy in the curved surface of the pores and the gas pressure in the pores [66]. For example, the pore shrinkage stops if the gas pressure trapped in the pores is larger than the surface energy on the surface of the pores. In our case, as shown in Figure 4.12, the equilibrium partial pressure of the component Mn in the ternary Fe-Mn-Si alloys was as high as 16.6 Pa. In other words, the pressure in the pores kept $\sim$16.6 Pa during isothermal holding. This inhibited the pore shrinkage, especially for the isolated pores, and consequently prevents the densification of the sintered compacts.
6.4.3 Fracture

As shown in Table 6.2, the mechanical properties of all the sintered PM alloys increased gradually with the increase of the isothermal holding time. The variation in mechanical properties is attributed to the different porosities of the sintered alloys, which is illustrated by the Gibson-Ashby model [228]. The Gibson-Ashby relationship demonstrates that both the tensile strength and modulus of elasticity of the PM alloys increase with the decrease of porosities. Figure 6.2 presented that the porosities of all the sintered alloys decreased with the increase of the isothermal holding. Therefore, the mechanical properties of the sintered alloys increased as isothermal holding time increases.

Figure 6.11 presents the SEM fractographies of the sintered Fe-Mn-Si alloys with various isothermal time. Shallow dimples were observed at the fracture surface of all the sintered alloys. This indicates that all the sintered alloys exhibited a typical ductile fracture. As shown in Figure 6.11, it is noted that the number of dimples was similar in all the sintered alloys. This again reveals that the increase of isothermal holding had a limited effect on the ductility of the Fe-Mn-Si compacts.

![Fractography of the MM Fe-Mn-Si compacts sintered at 1200°C for different isothermal holding times: (a) 1h, (b) 3h.](image)

Figure 6.11 Fractography of the MM Fe-Mn-Si compacts sintered at 1200°C for different isothermal holding times: (a) 1h, (b) 3h.
6.5 Conclusion

(1) The density of the sintered ternary Fe-Mn-Si alloys increased drastically in the first hour of the isothermal holding, while it increased slowly when the isothermal time is $>$1 h. A rapid drop in open porosities occurred in the compacts during the first hour of isothermal holding.

(2) The surface of the sintered ternary Fe-Mn-Si compacts was comprised of a single $\alpha$-Fe phase. The alloys in the regions $\geq$ MDR consisted of major $\gamma$-austenite and minor $\varepsilon$-martensite.

(3) The weight loss of the sintered ternary Fe-Mn-Si compacts with no isothermal holding was only $\sim$ 2%. The weight loss of the sintered Fe-Mn-Si compacts increased significantly to 7.65% after the first hour of isothermal holding. The weight loss was very limited when the isothermal holding was $>1$ h. The MDR region increased with the increase of isothermal time.

(4) Long isothermal holding ($>1$h) had a limited role in promoting the mechanical properties. All sintered compacts presented a typical ductile fracture.
Chapter 7 A comparative study of powder metallurgical and wrought Fe-Mn-Si alloys

This chapter is mainly extracted from the published work in Materials Science and Engineering A[202] and International Journal of Modern Physics B[203]. The purpose of this chapter is to compare mechanical properties and degradation performance of PM Fe-Mn-Si alloys to their casting counterparts.

7.1 Introduction

Permanent biomedical materials with high corrosion resistance, such as 316L stainless steels, titanium (Ti) alloys and cobalt-chromium (Co-Cr) alloys are widely used as implants for orthopaedic and cardiovascular applications [47, 230-232]. For decades, it has been believed that these implants with high corrosion resistance could not only maintain the mechanical integrity of implanted devices stable in the human body over the lifetime of implantation, but also prevent the release of non-compatible ions, to a large extent, from the implants in the human body. However, in certain cases, such as artery occlusion and some types of bone fracture, it has been realised that a degradable implant is more favourable than the permanent bio-inert counterpart [233]. Take artery occlusion for example, implanting a tiny and expandable stent is a widely adopted surgical procedure to re-open the blocked vessels. It is recognised that the healing process of blocked vessels could be completed in 6~12 months [16, 234, 235]. After the recovery of blocked vessels, the stent is no longer necessary and its presence indeed causes a series of potential long-term complications, such as chronic inflammation, possible later thrombosis, and systemic toxicity. A second surgical intervention for implant removal is therefore often required [12, 236]. Because of this, implants made of degradable biomaterials have become a promising alternative to overcome and minimise the complications caused by bio-inert materials.

Polymers are the first type of degradable biomaterials [161]. However, polymeric implants, by and large, have relatively low mechanical properties which limit them to non-load-bearing applications [237, 238]. Metallic degradable biomaterials including Fe-based alloys and Mg-based alloys with better mechanical properties, on the other hand, can meet the requirements
for mechanical properties [53, 166, 239-242]. Mg-based degradable alloys have been by far most extensively explored. However, the degradation rate of Mg biomaterials in a physiological environment is too fast to meet the requirements of applications such as cardiovascular stents and implants for osteosynthesis [243-245]. Equally or even more importantly, excessive hydrogen gas is generated during Mg degradation in the human body [246, 247]. By contrast, Fe-based alloys present a more reasonable degradation rate than Mg-based alloys, which is beneficial to the patient as they provide adequate mechanical integrity for diseased tissue until the completion of tissue healing [16, 127, 166, 180]. Therefore, Fe-based alloys have become an interesting and attractive alternative in recent years at an attempt of overcoming the drawbacks of both polymeric and Mg-based degradable biomaterials.

Recently, a ternary Fe-30Mn-6Si alloy was developed as a promising biodegradable material due to its high cell viabilities, low haemolysis, high mechanical properties and suitable degradation rate [38]. In this work, we intend to provide a complementary powder metallurgical study of such a Fe-Mn-Si alloy for the first time and compare it with the cast/wrought route. The investigation of the relationship between Si content and degradation rate in ternary Fe-Mn-Si alloys is very scarce and hence is another equally important objective of our present study.

## 7.2 Experimental procedures

### 7.2.1 Powder sintering

The starting powders used in this study were pure elemental Fe powder, Mn powder and Si powder. The chemical purity and particle size are listed in Table 3.4 (Chapter 3), while the morphologies of these powders are shown in Figure 3.2 (Chapter 3). The powder mixture of Fe-28 wt.%Mn with Si of 0, 1, 2, 3 or 4 wt.% was subject to dry milling in a Fritsch planetary mill for 5 h, at a rotation speed of 275 rpm and a ball-to-powder weight ratio of 5:1.

The as-milled Fe-28Mn-xSi (wt.%, x = 0, 1, 2, 3, 4) powder mixture was uniaxially pressed in a steel die into rectangular compacts (40 × 16 × 4.2 mm³) under a compaction pressure of 400 MPa. Subsequently, all the green compacts were sintered in a vacuum furnace at 5×10⁻
3 Pa. The heating profile for sintering is sketched in Figure 7.1, where the heating rate was 10 °C/min at T < 800 °C and 5 °C/min at above 800 °C. The final sintering was carried out at 1200 °C for 3 h. Figure 7.2 presents the as-sintered Fe-Mn-based alloys (PM alloys or PM samples hereafter) and a tensile bar cut from the as-sintered alloys. Results in previous Chapters 4, 5 and 6 have demonstrated that Mn depletion regions (~ 500 μm) were exited on the surface of all the compacts sintered for 3 h at 1200 °C. It is pointed out that the Mn depletion regions were removed from the sintered samples for all the testings and characterisations in this chapter.

Figure 7.1 Heating profile for vacuum sintering of Fe-Mn-xSi alloys.
7.2.2 Casting and forging

Three Fe-Mn-xSi (x = 0, 2 and 4 wt.%) alloys were melted in a vacuum arc-melting furnace. The casting procedures for making button samples were presented in Chapter 3. All button castings were subsequently homogenized at 1100°C for 8 h in vacuum and cooled inside the furnace to room temperature. Then, the as-homogenised buttons were forged at 1000 °C by open die forging with a forging ratio of 3:1. A macroscopic view of the as-cast button and as-forged disk is shown in Figure 7.3. The chemical compositions of the above prepared samples via either powder sintering or casting/forging are listed in Table 7.1, which confirms that the loss of Mn during melting or sintering was insignificant.
Figure 7.3 Macroscopic images of wrought Fe-Mn-xSi alloys: (a) as-cast and (b) as-forged.

Table 7.1 Chemical compositions (wt. %) of the fabricated alloys.

<table>
<thead>
<tr>
<th>Fabrication method</th>
<th>Material</th>
<th>Chemical composition (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>Powder sintering</td>
<td>Fe-28Mn</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe-28Mn-1Si</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe-28Mn-2Si</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe-28Mn-3Si</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe-28Mn-4Si</td>
<td>Bal.</td>
</tr>
<tr>
<td>Casting &amp; forging</td>
<td>Fe-28Mn</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe-28Mn-2Si</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe-28Mn-4Si</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
7.2.3 Electrochemical analysis

Details on the procedures of the electrochemical analysis have been presented in Chapter 3.

7.2.4 Microstructural characterization and mechanical test

For methods on microstructure observation, phase identification and mechanical test refer to Chapter 3.

7.3 Results

7.3.1 Microstructure observation

Figure 7.4 shows the SEM micrographs of the as-sintered alloys with various Si contents. A large number of elongated pores are visible and most of them are of irregular shape. This is a typical sintered microstructure. It is noted that the pores in the ternary alloys with 3 and 4 wt.% Si are apparently smaller than the other alloys with lower, or no Si content. In addition, the number of pores decreases with increasing Si content (Figure 7.4). In other words, Si promotes powder densification.
Figure 7.4  Microstructure of as-sintered Fe-28Mn-xSi alloys: (a) Fe-28Mn, (b) Fe-28Mn-1Si, (c) Fe-28Mn-2Si, (d) Fe-28Mn-3Si, (e) Fe-28Mn-4Si.
All Fe-Mn-xSi castings demonstrate coarse cast microstructure (not shown here). After hot forging, these coarse grains were significantly refined. Figure 7.5 presents the forged microstructures in the Fe-Mn-xSi alloys. In general, all these forged samples show fine equiaxed austenite grains. The average grain size of the as-forged binary Fe-28Mn alloy is approximately 50μm, while it is ~30μm, i.e., 40% reduction in the ternary alloys. In addition, many thin martensitic plates are clearly visible in the Fe-28Mn-4Si alloy grains.

Figure 7.5 Optical micrographs of as-forged Fe-28Mn-xSi alloys: (a) Fe-28Mn, (b) Fe-28Mn-2Si, (c) Fe-28Mn-4Si.

7.3.2 Phase identification

Figure 7.6 illustrates the XRD patterns of the as-sintered Fe-28Mn-xSi compacts. The as-sintered samples with Si content ≤ 2 wt.% consist of a single γ-austenite phase. In the sintered
Fe-28Mn-3Si and Fe-28Mn-4Si alloys, a weak diffraction peak, which can be indexed to ε-martensite phase, was detected, in addition to the dominant γ-austenite phase. No α-Fe or Mn phase was identified. This indicates that fully alloying was achieved after sintering at 1200 °C for 3 h.

XRD patterns of the wrought Fe-28Mn-xSi samples after forging are presented in Figure 7.7. In addition to γ austenite, strong peaks from ε martensite phase were also observed in the Fe-28Mn-2Si and Fe-28Mn-4Si alloys. This implies that Si promoted the stress-induced martenstic transformation.

Figure 7.6 XRD pattern of the as-sintered Fe-28Mn-xSi alloys: (a) Fe-28Mn, (b) Fe-28Mn-1Si, (c) Fe-28Mn-2Si, (d) Fe-28Mn-3Si, (e) Fe-28Mn-4Si.
7.3.3 Density and porosity of PM samples

The relative density of green and as-sintered compacts is shown in Figure 7.8. It can be seen that the green density decreases with Si content. For example, the relative density of the Fe-28Mn-4Si green compacts was ~62.9%, while that of the Fe-28Mn compacts was 67.7%. After sintering, all the Fe-28Mn-xSi compacts attained a similar sintered density, regardless of the Si content. The densification level of each compact is superimposed in Figure 7.8, which shows densification increased significantly with Si content.
Figure 7.8 Relative density of green compacts and as-sintered samples as a function of Si content. (The bars on the data represent the highest and lowest density reported in each group of samples.)

7.3.4 Static tensile test

Figure 7.9 and Figure 7.10 illustrate typical tensile engineering stress-strain curves of both the as-sintered and as-forged samples with various Si contents. The mechanical property data derived from these curves are tabulated in Table 7.2 and Table 7.3 respectively. Some important observations can be made. The tensile strength of the as-sintered alloys increased with the increase of Si content. For instance, a 3-fold increase in ultimate tensile strength (UTS) was observed in Fe-28Mn-4Si, as compared to the Si-free Fe-28Mn alloy (from 180 MPa for Fe-28Mn to 373 MPa for Fe-28Mn-4Si, Table 7.2). Young’s modulus gradually increased with Si content, up to ~87 GPa in the Fe-28Mn-4Si alloy. It is noted that all of the sintered samples demonstrated a relatively low elongation of ~7.3% (Table 7.2).
In the case of the as-forged samples, UTS increased gradually while ductility decreased sharply with increasing Si content (Table 7.3). For example, the forged Fe-28Mn-4Si had UTS of ~850 MPa, 25% higher than that of Si-free Fe-28Mn, while its ductility was reduced by three times. The elastic moduli of all these forged alloys were nearly identical (~160GPa). In comparison to the powder sintered samples, all of the forged samples had much higher strength and ductility, as a result of a fully dense and much finer microstructure in the forged alloys.

Figure 7.9  Tensile stress-strain curves of Fe-28Mn-xSi alloys after sintering at 1200°C for 3h: (a) Fe-28Mn, (b) Fe-28Mn-2Si, (c) Fe-28Mn-4Si.
Table 7.2  Static tensile properties of the as-sintered Fe-Mn-based alloys.

<table>
<thead>
<tr>
<th>Sintered sample</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Fracture strain (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-28Mn</td>
<td>180 ± 17.2</td>
<td>7.58 ± 1.15</td>
<td>75.35 ± 3.21</td>
</tr>
<tr>
<td>Fe-28Mn-1Si</td>
<td>186.6 ± 12.4</td>
<td>7.31 ± 0.69</td>
<td>77.97 ± 2.43</td>
</tr>
<tr>
<td>Fe-28Mn-2Si</td>
<td>195 ± 11.8</td>
<td>7.35 ± 0.72</td>
<td>79.65 ± 3.11</td>
</tr>
<tr>
<td>Fe-28Mn-3Si</td>
<td>331 ± 24.3</td>
<td>7.42 ± 1.02</td>
<td>81.28 ± 2.37</td>
</tr>
<tr>
<td>Fe-28Mn-4Si</td>
<td>373 ± 32.1</td>
<td>7.28 ± 0.53</td>
<td>86.79 ± 2.89</td>
</tr>
</tbody>
</table>

Figure 7.10  Tensile stress-strain curves of the forged Fe-28Mn-xSi alloys, (a) Fe-28Mn, (b) Fe-28Mn-2Si and (c) Fe-28Mn-4Si.
Table 7.3 Static tensile properties of the as-forged Fe-Mn-based alloys.

<table>
<thead>
<tr>
<th>Forged sample</th>
<th>Ultimate tensile strength/MPa</th>
<th>Fracture strain /%</th>
<th>Young’s modulus( GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-28Mn</td>
<td>682.48</td>
<td>40.41</td>
<td>158</td>
</tr>
<tr>
<td>Fe-28Mn-2Si</td>
<td>790.64</td>
<td>26.9</td>
<td>160.76</td>
</tr>
<tr>
<td>Fe-28Mn-4Si</td>
<td>847.55</td>
<td>13.63</td>
<td>163.58</td>
</tr>
</tbody>
</table>

7.3.5 Degradation properties

The potentiodynamic polarization curves of the as-sintered alloys are presented in Figure 7.11. Degradation (corrosion) current density measured by polarization resistance method is summarized in Table 7.4. In general, the corrosion current density decreased with increasing Si content, while the corrosion potentials are similar for all these sintered samples. Figure 7.12 shows the potentiodynamic polarization curves of the as-forged fully dense samples and Table 7.5 summarises the corrosion current density and corrosion potential. Interestingly, the corrosion current density of the as-forged samples increased with Si content, while the corrosion potential was very similar for all of the forged samples. Comparing the potentiodynamic data revealed that each of the as-forged samples had a much lower current density than its sintered counterpart, regardless of Si content.
Figure 7.11 Potentiodynamic polarization curves of the sintered Fe-28Mn-xSi alloys.

Table 7.4 Corrosion properties of as-sintered Fe-28Mn-xSi alloys.

<table>
<thead>
<tr>
<th>Material</th>
<th>$I_{\text{Corr}}$ (μA/cm$^2$)</th>
<th>Corrosion potential (mv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-28Mn</td>
<td>54.8±8.5</td>
<td>-899±71</td>
</tr>
<tr>
<td>Fe-28Mn-1Si</td>
<td>47.9±3.6</td>
<td>-902±65</td>
</tr>
<tr>
<td>Fe-28Mn-2Si</td>
<td>42±4.1</td>
<td>-901±69</td>
</tr>
<tr>
<td>Fe-28Mn-3Si</td>
<td>37.5±3.8</td>
<td>-892±73</td>
</tr>
<tr>
<td>Fe-28Mn-4Si</td>
<td>35.5±2.7</td>
<td>-904±62</td>
</tr>
</tbody>
</table>
Figure 7.12  Potentiodynamic polarization curves of the as-forged Fe-28Mn-xSi alloys.

Table 7.5  Corrosion properties of as-forged Fe-28Mn-xSi alloys.

<table>
<thead>
<tr>
<th>Material</th>
<th>$I_{corr}$(μA/cm$^2$)</th>
<th>Corrosion potential(mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe28Mn</td>
<td>15.8±2.5</td>
<td>-806±65</td>
</tr>
<tr>
<td>Fe-28Mn-2Si</td>
<td>18.2±2.3</td>
<td>-816±67</td>
</tr>
<tr>
<td>Fe-28Mn-4Si</td>
<td>21.1±2.6</td>
<td>-816±63</td>
</tr>
</tbody>
</table>
7.4 Discussion

7.4.1 Effect of Si on powder densification

As shown in Figure 7.8, the addition of Si decreases the green density of the pressed compacts, because the hard Si particles are more difficult to compact than ductile Fe and Mn particles [248], therefore decreasing the overall powder compactibility. However the densification of the Fe-Mn-Si compacts increased with Si (Figure 7.8) and the number and size of macropores in the sintered samples decreased with Si content. This increased densification may be attributed to the formation of a transient liquid phase during sintering. According to the ternary Fe-Mn-Si phase diagram [249], the liquid phase forms at ~ 1040 °C in Fe-28Mn-4Si, much lower than the liquid phase forming temperature in the binary Fe-28Mn alloy (~1246 °C). At the sintering temperature of 1200 °C, the formation of the liquid phase in the ternary alloys accelerated diffusion of Mn into Fe matrix, leading to a higher level of densification in these ternary alloys. On the contrary, densification in binary Fe-28Mn alloy at 1200 °C was through solid-state diffusion.

7.4.2 Tensile properties and fracture behaviour

As shown in Table 7.2 and 7.3, the UTS for both sintered and forged samples increased with increasing Si content. This is because Si dissolves into the Fe matrix and forms a solid solution [250, 251], which results in solid solution strengthening of the austenitic γ phase. Therefore, a higher tensile strength is obtained in ternary Fe-Mn-Si alloys, as compared to Si-free binary alloys. Moreover, in a solid solution, yield strength increases approximately parabolically with solute content within the solubility range [252]. It is noted that the amount of Si addition in our study was far below the solubility of Si in Fe (~10 wt.% [253]). For the same reason, ductility reduced with Si content.

In the powder sintered alloys, the porosity also makes an important contribution to the tensile strength of Fe-Mn-based alloys. In general, the presence of pores leads to a reduction in the effective load-bearing cross-sectional area, and hence lowers the mechanical strength. In our case, a porosity of 15% to 20% was observed in the as-sintered samples, which resulted in a
significant reduction in UTS and ductility, when compared to the fully dense forged counterparts.

In the forged alloy samples, the presence of martensite might also reduce the ductility of Fe-Mn alloys. Figs. 7.5 and 7.7 reveal that the amount of martensite phase in the as-forged alloys increased with Si content. Therefore, Fe-28Mn-4Si forged alloy had a lower ductility than the other samples.

As a consequence of incomplete densification, the sintered samples demonstrated a mixture of ductile and brittle fracture surface, as shown in Figure 7.13. Powder particle detachment is visible; however a close-up observation of the fracture surface reveals some dimples within γ-austenite grains (See Figure 7.13 (d)). In all of the fractured samples, many voids (sintered pores) are visible on the fracture surface. In comparison, a typical ductile fracture was observed in the forged samples, as evidenced by numerous dimples. It is interesting to note that the size and depth of the dimples varies with different Si content in the as-forged samples. A lower Si content in the sample corresponds to larger and deeper dimples and higher ductility in the alloys.
Figure 7.13 Fracture surfaces of the as-sintered Fe-28Mn-xSi alloys sintered at 1200 °C. (a) Fe-28Mn, (b) Fe-28Mn-2Si, (c) Fe-28Mn-4Si, (d) enlarged square area in (c).
Figure 7.14 Fracture surfaces of the as-forged Fe-28Mn-xSi alloys: (a) Fe-28Mn, (b) Fe-28Mn-2Si, (c) Fe-28Mn-4Si.

7.4.3 Corrosion performance

The electrochemical results show that an increase in Si content resulted in an increase in corrosion current density for the fully dense forged alloys (Table 7.5). This observation is different from other reports in the literature. It has been reported that Si could be incorporated into Fe₂O₃ film to form a more stable surface layer so as to decrease the corrosion rate of Si-containing Fe-Si, Fe-Cr-Si and Fe-B-Si alloys [254-256]. The observed increase in degradation rate with Si in the present study might be caused by the presence of multiple phases. In general, a duplex-phase alloy corrodes faster than a single-phase counterpart, because additional galvanic corrosion occurs in the duplex-phase alloys [127, 257]. As shown
in the XRD patterns of the forged alloys (Figure 7.7), the Si-containing ternary alloys are comprised of a dominant ε-martensite and minor γ-austenite phases. This duplex phase microstructure is expected to generate considerable galvanic corrosion sites between them, therefore increasing corrosion susceptibility. By contrast, with a single γ-austenite phase, the Si-free binary alloy only experiences uniform corrosion. In ternary alloys, it appears that galvanic corrosion outperforms the Si stabilisation of Fe₂O₃ films.

In the case of the PM porous samples, the degradation rate decreased with Si. The Si incorporation to the Fe₂O₃ film could contribute to the reduced corrosion; however, the reduced degradation was mainly caused by the reduced porosity in the Si-containing ternary alloys. A reduced porosity not only decreases the exposure area, but also decreases the possibility of crevice corrosion.

### 7.5 Conclusion

In this study a series of Fe-Mn-Si alloys as degradable biomaterials were synthesised via both powder sintering and casting/forging. The following conclusions can be drawn:

1. The alloys fabricated via powder metallurgy (PM) had a relatively high porosity ranging from 17.5% to 20%. The powder densification increased significantly with increasing Si content. The PM alloys with Si content no more than 2 wt.% are comprised of a single γ-austenite phase. If the Si content was ≥3 wt.%, the powder sintered alloys consisted of a major γ-austenite phase and a minor ε-martensite phase. With an increase in Si content, the tensile strength dramatically increased while modulus of elasticity increased only mildly. The PM samples demonstrated a mixture of ductile and brittle fracture surface.

2. Si affects the phase constituents in the wrought alloys. In Si-free binary Fe-28Mn alloy only γ-austenite phase exists, while the ternary Fe-Mn-Si alloys consist of duplex γ-austenite and stress-induced ε-martensite phases. The tensile strength of the wrought alloys increased with Si content, while modulus of elasticity remained unchanged regardless of Si content. The wrought alloy samples fractured in a typical ductile mode and the ductility reduced
drastically with Si content. In comparison to the PM Fe-Mn-Si alloys, the wrought alloys had considerably higher mechanical properties.

(3) The degradation rate largely depends on the amount of Si, but the dependence is different for PM alloys and wrought alloys. In the PM alloy samples, the degradation rate decreased with Si content. On the contrary, in the wrought alloys the degradation rate increased with Si content. In general, the PM alloys presented a higher degradation rate than their wrought counterparts, due to the porosities in the PM alloy samples.
Chapter 8 Effect of immersion on the mechanical properties and biocompatibility of the sintered Fe-Mn-based alloys

8.1 Introduction

As summarised in Chapter 2, Fe-Mn-based degradable biomaterials are commonly designed for implants such as cardiovascular stents and load bearing implants such as bone fixation devices. In this case, mechanical properties therefore are essential indicators that should be considered when designing Fe-Mn-based DBMs for load-bearing applications. Degradable devices implanted in the human body are exposed to an aggressive physiological environment. This leads to the degradation of the implanted devices and therefore the decrease of mechanical properties. As illustrated in Chapter 2, a variety of static mechanical tests have implied that the mechanical properties of the fabricated Fe-Mn-based DBMs are adequate to support the healing of diseased tissues. However, it is noted that most of the mechanical tests ignored the implantation time dependence of mechanical properties of Fe-Mn-based DBMs in a physiological environment. It is believed that current available data on mechanical properties cannot reflect the real mechanical properties of the implanted Fe-Mn-based DBMs after serving in the human body for a certain period. The decrease of mechanical properties seriously affects the life span of the served degradable implants. This is because the decrease of mechanical properties could finally make the degradable implants lose their mechanical integrity. Therefore, it is important to establish the relationship between mechanical properties of Fe-Mn-based DBMs and the implantation time in order to better predict the life span of the designed Fe-Mn-based DBMs.

The immersion test is considered an effective way to simulate and predict the implantation time dependence of mechanical properties of Fe-Mn-based DBMs. In this chapter, the mechanical properties of the sintered Fe-Mn-based alloys were investigated as a function of immersion time in SBF solution. In addition, the biocompatibility of the sintered Fe-Mn-based alloys was evaluated.
8.2 Experimental

Most of the experimental procedures were described in Chapter 3. The following section only details the experimental procedures which are not presented in Chapter 3. Results in previous Chapters 4, 5 and 6 have demonstrated that Mn depletion regions (~ 500 μm) were exited on the surface of all the compacts sintered for 3 h at 1200 °C. It is pointed out that the Mn depletion regions were removed from the sintered samples for all the testings and characterisations in this chapter.

8.2.1 Immersion test

Immersion testing of all the sintered samples were conducted in the simulated body fluid (SBF) according to ASTM-G31-12a, which is listed in Table 3.2. All the samples in this chapter were immersed in 30 ml of SBF solution in a water bath at 37°C. Two types of samples were used for the immersion test. One is tensile bar as specified in Section 3.4.3; the other is rectangular samples for ion concentration measurement, and the sequent cytotoxicity test. For the tensile bars, a wide range of immersion times including 15 days, 30 days, 45 days and 60 days were selected. In the case of the rectangular samples, the samples were mounted in epoxy resin before immersion, and ground with silicon carbide papers up to 1200 grit. The surface area of the specimens exposed to SBF solution during immersion test was 1 x 1 cm². The immersion duration for the rectangular sample in the SBF solution was 7 days. After 7 day immersion, the SBF solutions dissolved with Fe and Mn ions were diluted by 20 times. The concentration of Fe and Mn ions in the diluted SBF solutions was measured using inductively coupled plasma-mass spectrometry (ICP-MS). The cell viability was measured at 530 nm excitation and 590 nm emission using a Perkin Elmer Enspire 2300 Multibabel Reader.

8.3 Results and discussion

8.3.1 Mechanical properties of the immersed Fe-Mn-based alloys

Figure 8.1 illustrates the engineering stress-strain curves of the immersed Fe-28Mn-based specimens. All curves presented characteristic strain hardening. The ultimate tensile strength
(UTS) and fracture strain ($\varepsilon$) of all the immersed samples are summarised in Table 8.1. In general, the UTS and $\varepsilon$ decreased with increasing immersion time for both ternary and binary specimens. A significant decrease in UTS of the ternary Fe-Mn-Si specimens occurred when the immersion period $\geq 45$ days. In detail, the UTS of the ternary samples immersed for 30 days reduced by $\sim 4.2\%$ compared to their counterparts with no immersion, while that for 45 days and 60 days decreased by $\sim 16.6\%$ and $45\%$, respectively. By contrast, immersion time had less influence on the UTS of the binary Fe-Mn specimens compared to their ternary Fe-Mn-Si counterparts. For instance, the UTS of the binary Fe-Mn specimens immersed for 60 days decreased by $28.2\%$ compared to their counterparts with no immersion. This is far less than that of the ternary Fe-Mn-Si counterparts ($45\%$). Interestingly, the $\varepsilon$ evolution of both the binary Fe-Mn and ternary Fe-Mn-Si alloys exhibited a similar trend to that of the UTS. For instance, the $\varepsilon$ of the ternary Fe-Mn-Si specimens immersed for 45 days was $1.93\%$, only $\sim 1/5$ of the samples with no immersion. However, it is noted that immersion time presented a more significant effect on degrading the $\varepsilon$ compared to UTS.

The mechanical properties of the immersed Fe-Mn-based samples are determined by their microstructure. Figure 8.2 shows the surface morphologies of the sintered Fe-Mn-based samples with different immersion durations. A comparison of Figure 8.2 (a) and Figure 8.2 (d) with Figure 8.2 (b) and Figure 8.2 (e) illustrates that the surface morphologies of the samples immersed for 15 days, in general, is similar to that with no immersion. In detail, uniform corrosion occurred on the surface of all samples immersed for 15 days. Thus, the mechanical properties of the samples immersed for 15 days are comparable to those with no immersion.

As shown in Table 8.1, the mechanical properties, especially the fracture strain of the sintered Fe-Mn-Si significantly degraded. This may be caused by the large localised pits formed in the ternary Fe-Mn-Si samples. Large pits were observed on the surface of the ternary Fe-Mn-Si samples after being soaked for 45 days, as shown in Figure 8.2 (c). These severely localised large pits are weak sites for crack initiation, and therefore lead to the deterioration in the mechanical properties of the sintered Fe-Mn-Si alloys.

Figure 8.2 (f) reveals that the pores of the binary Fe-Mn samples immersed for 45 days became much larger than their counterparts with no immersion. These enlarged pores
significantly decreased the effective load-bearing area, and hence degraded the mechanical properties. However, it is pointed out that no pits were observed on the surface of the binary Fe-Mn samples immersed for 45 days. In other words, uniform corrosion occurred in the pore-free area of the binary Fe-Mn samples. According to the above results, the reduced mechanical properties of the binary Fe-Mn samples after immersing for 45 days may be attributed to the enlarged pores. The higher mechanical properties of the binary Fe-Mn samples immersed for 45 days compared to their ternary Fe-Mn-Si counterparts, benefit from their pitting-free microstructure.

The weak mechanical properties of both the binary Fe-Mn and ternary Fe-Mn-Si samples after long time immersion can be also reflected in their fractography. Figure 8.3 (b) and Figure 8.3 (d) show that dimples in both samples immersed for 45 days decreased remarkably with respect to their counterparts with no immersion. This firmly proved the inferior mechanical properties of both binary and ternary samples immersed for a long time (≥45 days).

Figure 8.1  Tensile stress-strain curves of sintered Fe-28Mn-based alloys immersed in SBF solution for various durations: (a) Fe-28Mn-3Si alloys immersed for 15 days, (b) Fe-28Mn-3Si alloys immersed for 30 days, (c) Fe-28Mn-3Si alloys immersed for 45 days, (d) Fe-
28Mn-3Si alloys immersed for 60 days, (e) Fe-28Mn alloys immersed for 15 days, (f) Fe-28Mn alloys immersed for 30 days, (g) Fe-28Mn alloys immersed for 45 days, (h) Fe-28Mn alloys immersed for 60 days (i) Fe-28Mn-3Si alloys with no immersion, (j) Fe-28Mn alloys with no immersion.

Table 8.1 Tensile properties of the sintered Fe-28Mn-based alloys immersed in SBF solution for various durations.

<table>
<thead>
<tr>
<th>Type of powder mixture</th>
<th>Immersion time (Day)</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Fracture strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-28Mn-3Si</td>
<td>0</td>
<td>337.2±15.6</td>
<td>9.2±0.73</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>334.5±12.3</td>
<td>6.62±0.56</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>323.5±11.2</td>
<td>5.65±0.52</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>281.3±12.5</td>
<td>1.93±0.36</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>186.6±9.7</td>
<td>0.92±0.38</td>
</tr>
<tr>
<td>Fe-28Mn</td>
<td>0</td>
<td>245.8±13.5</td>
<td>9.36±0.66</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>229.9±12.9</td>
<td>6.15±0.52</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>216.7±11.2</td>
<td>6.12±0.55</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>197.9±13.4</td>
<td>4.32±0.39</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>176.5±9.66</td>
<td>3.75±0.38</td>
</tr>
</tbody>
</table>
Figure 8.2 SEM micrographs of the sintered Fe-28Mn-based alloys immersed in SBF solution for different durations: (a) Fe-28Mn-3Si alloy with no immersion, (b) Fe-28Mn-3Si alloys immersed for 15 days, (c) Fe-28Mn-3Si alloys immersed for 45 days, (d) Fe-28Mn alloy with no immersion, (e) Fe-28Mn alloys immersed for 15 days, (f) Fe-28Mn alloys immersed for 45 days.
Figure 8.3  Fracture surfaces of the as-sintered Fe-28Mn-based alloys immersed in SBF solution for different durations: (a) Fe-28Mn-3Si alloy with no immersion, (b) Fe-28Mn-3Si alloys immersed for 45 days, (c) Fe-28Mn alloys without immersion, (d) Fe-28Mn alloys immersed for 45 days.
8.3.2 Biocompatibility of the sintered Fe-Mn-Si alloys

Figure 8.4  Concentration of Fe and Mn ions released from the sintered Fe-28Mn and Fe-28Mn-3Si alloys immersed in SBF solutions for 7 days.

Figure 8.4 presents the Fe and Mn ion concentration releasing into the SBF solution after the bulk samples were soaked for 7 days. The Fe and Mn ion concentration released from the ternary Fe-Mn-Si samples was ~0.392 and 0.13 ppm, respectively. Interestingly, the Fe ion concentration released from the binary Fe-Mn samples was almost equal to that from the ternary Fe-Mn-Si samples. However, the Mn ion concentration released from the binary alloys was only around 55% of that from the ternary alloys. This reveals that the ion release rate of the ternary Fe-Mn-Si samples in SBF solution is faster than their binary Fe-Mn counterparts. This agrees with the electrochemical results shown in Chapter 4. Figure 8.5 shows the results of the in vitro cytotoxicity test. It can be seen that fluorescence values of both ternary Fe-Mn-Si and binary Fe-Mn samples increased with the increase of culture time. In other words, the released ions from both the binary and ternary bulk samples did not inhibit the proliferation of L929 cells. This confirms that the sintered Fe-Mn-based alloys present a good viability in L929 cells.
In this chapter, the mechanical properties of the sintered Fe-Mn-based samples immersed in SBF solutions were investigated. In addition, the biocompatibility of the sintered Fe-Mn-based alloys was assessed using SBF solution immersed with sintered bulk Fe-Mn-based alloys. In general, the mechanical properties decreased with the increase of immersion time. A severe decrease in mechanical properties occurred in both binary Fe-Mn and ternary Fe-Mn-Si samples after being immersed for ≥ 45 days. However, it is clear that the binary Fe-Mn samples present better mechanical properties than their binary Fe-Mn-Si counterparts under the same immersion duration. The number of Mn ions released from the ternary Fe-Mn-Si samples was much higher than their binary Fe-Mn counterparts. The cytotoxicity test suggests that both the ternary Fe-Mn-Si and binary Fe-Mn alloys present no inhibition on the proliferation of L929 cells.
Chapter 9  Conclusions and Future work

This chapter summarises the key findings from this research and provides several recommendations for future research.

9.1 Conclusions

In this thesis, Fe-Mn-Si alloys proposed as degradable biomaterials (DBMs) were fabricated via powder metallurgy (PM). Fe-Mn-Si alloy with an optimal Si content was determined under a comprehensive consideration on mechanical properties and degradation performance. The influences of mechanical milling, sintering temperature and isothermal time on densification, mechanical properties and Mn sublimation were systematically evaluated. In addition, the biocompatibility and immersion time dependence of the mechanical properties of the PM Fe-Mn-Si alloys were assessed. In general, the following conclusions can be drawn.

Fe-Mn-Si alloys with various Si content were synthesised via both powder sintering and casting/forging. It was found that the degradation rate largely depends on the amount of Si content. The degradation rate of the PM Fe-Mn-Si alloys decreased with Si content. The porosities in the PM alloys were favoured to obtain a higher degradation rate. The powder densification increased significantly with increasing Si content. With an increase in Si content, the tensile strength dramatically increased while modulus of elasticity increased only mildly. Based on the above findings, the PM Fe-28Mn-3Si alloy (in weight percent) was selected for further investigation.

The effects of mechanical milling and sintering temperature on the microstructure evolution, densification, mechanical properties and Mn sublimation of the sintered Fe-28Mn-3Si alloys were reported. No densification occurred in the BE alloys at all sintering temperatures. The density of the MM alloys increased drastically with the increase of sintering temperature (from ~67% at 1000 °C to ~85% at 1200 °C). The open porosities of the BE alloys was significantly higher than their MM counterparts. Predominant γ-austenite and minor ε-martensite were identified in the BE alloys if sintering temperature was ≤1200 °C. It is pointed out that a large amount of Mn$_3$Si intermetallic phase formed in the BE alloys sintered
at 1000 °C. However, only a single α-Fe phase was found in the BE compacts sintered at 1300 °C. The MM alloys were comprised of predominant γ-austenite and minor ε-martensite at all sintering temperatures. The pore size of MM alloys decreased significantly with the increase of sintering temperature, while a large number of pores with size ~150µm were formed in BE alloys when sintering temperature was ≥ 1200 °C. In general, the mechanical properties of both BE and MM alloys increased with increasing sintering temperature. The strength and ductility of the MM alloys, were remarkably higher than their BE counterparts. Both the sintered BE and MM samples exhibited a Mn depletion region (MDR) on the surface. The Mn concentration gradually increased with the increase of the distance from the surface (x=0) until it stabilizes at ~ 27wt.% when the distance was ≥ MDR. The thickness of the MDR layer increased with the increase of sintering temperature. The MDR thickness of the sintered BE compacts was significantly larger than their MM counterparts at the same sintering temperature. The weight loss of all the sintered compacts was mainly caused by the sublimation of Mn, and it increased significantly with the increase of sintering temperature. The weight loss of the MM alloys was much lower than their BE counterparts.

Fe-Mn-Si alloys sintered at 1200°C for various isothermal time were prepared. The effect of isothermal time on the densification, mechanical properties and Mn sublimation was systematically investigated. The results revealed that the density of the sintered ternary Fe-Mn-Si alloys increased drastically in the first hour of the isothermal holding, while it increased slowly when the isothermal time was >1 h. The weight loss of the sintered ternary Fe-Mn-Si compacts with no isothermal holding was only ~ 2%, and this increased by 3-fold after the first hour of isothermal holding. The MDR region increased with the increase of isothermal time. Long isothermal holding (>1h) played a limited role in promoting the mechanical properties.

The mechanical properties of the sintered Fe-Mn-based samples immersed in SBF solutions were investigated. In addition, the biocompatibility of the sintered Fe-Mn-based alloys was assessed using SBF solution to immerse the sintered Fe-Mn-based alloys. In general, the mechanical properties of the soaked samples decreased with the increase of immersion time. A severe decrease in mechanical properties occurred in both Fe-Mn and Fe-Mn-Si samples after being immersed for ≥ 45 days. The number of Mn ions released from the Fe-Mn-Si samples was much higher than their Fe-Mn counterparts. The cytotoxicity test suggested that...
both the Fe-Mn-Si and Fe-Mn alloys presented no inhibition on the proliferation of L929 cells.

9.2 Future work

In this thesis, PM Fe-Mn-Si alloys proposed as DBMs were fabricated using elemental Fe, Mn and Si powders. The results in previous chapters have confirmed the feasibility of the PM route to synthesise Fe-Mn-Si alloys as DBMs. The investigation of Fe-Mn-Si alloys as degradable biomaterials involves the degradation behaviour and mechanical performance, as well as biocompatibility. In the future, much work needs to perform in order to further adjust the degradation rate and evaluate the biocompatibility of PM Fe-Mn-Si alloys.

(1) A suitable degradation rate is always essential for degradable biomaterials. A low degradation rate is a common challenge for all the currently investigated Fe-based DBMs. Results in this thesis have presented an improved degradation rate of Fe-Mn-Si alloys compared to their Fe-Mn counterparts. However, the available degradation rate of Fe-Mn-Si alloys still cannot match the requirement for applications in the human body. For further research, increasing open porosities may be an effective way to upgrade the degradation rate. Additional open pores in the sintered alloys provide more areas for degradation, and therefore increase the degradation rate.

(2) Fe powders in the ball milled Fe-Mn-Si powder mixture failed to refine. The morphologies of the Fe-Mn-Si powder mixtures in previous chapters reveals that Fe powder presented a large elongated shape due to good ductility of pure Fe powders. Powders with large size are detrimental to densification. Moreover, coarse powders significantly prolong sintering time for the diffusion of the powders. In this case, more brittle Fe-Mn master powders may be an alternative to replace the pure iron powder in order to obtain Fe-Mn-Si powder mixtures with finer particle size.

(3) Fe-Mn-Si alloys are regarded as promising candidates for shape memory alloys. In next stage, it is worth studying the shape memory effect of the PM Fe-Mn-Si alloys by thermo-mechanical treatment.
(4) More investigations on the electrochemical behaviour of the PM Fe-Mn-Si alloys are required in order to obtain a comprehensive understanding on the degradation performance of the PM Fe-Mn-Si alloys. In this research, only Tafel plot was employed to assess the degradation rate. Electrochemical techniques such as cyclic voltammogram and Electrochemical Impedance Spectroscopy (EIS) are welcome to further reveal the degradation mechanism of the PM Fe-Mn-Si DBMs.

(5) It is recognised that Fe-Mn-Si DBMs, as degradable implants for load-bearing applications, are exposed to an environment surrounded by both low mechanical stress and corrosive body fluid. Stress corrosion commonly occurs during the implantation of the load-bearing medical devices. The stress applied in the human body may cause stress corrosion cracking (SCC), and consequently leads to the fracture of the implants. In this case, a stress corrosion crack (SCC) test is strongly recommended to be carried out in order to reveal the stress dependence of crack initiation and propagation.

(6) A longer time for the immersion test is necessary to obtain an accurate long term ion release rate of the PM Fe-Mn-Si alloys. In addition, direct contact cytotoxicity, the hemolysis test and the platelet adhesion test are required to further verify the in vitro biocompatibility of the PM Fe-Mn-Si alloys.
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