SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

POROUS MAGNESIUM USING POLYMETHYL METHACRYLATE (PMMA) AS A SPACE HOLDER FOR BIOMEDICAL APPLICATION

By

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Dissertation submitted in partial fulfillment

of the requirements for the degree of Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

JUNE 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “**Porous Magnesium Using Polymethyl Methacrylate (PMMA) As A Space Holder For Biomedical Application**”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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ACKNOWLEDGEMENTS

I would like to take this opportunity to express a deep sense of gratitude and sincere thanks to my supervisor, Dr. Anasyida Bt. Abu Seman and co-supervisor, Dr. Nurazreena Bt. Ahmad. I really appreciate the effort and time my supervisor spent in guiding and encourage me throughout the research. Her guidance helped me in all the time of research and writing of this thesis. Moreover, my sincere thanks also go to University Science Malaysia (USM) and School of Materials and Mineral Resources Engineering for providing me comfortable workplace and sufficient equipment to complete this research.

In addition, this thesis would not be achievable without substantial support from all the laboratory and workshop technicians, especially Encik Mohamad Shafiq Bin Mustapa Sukri, Encik Mokhtar Bin Mohamad, Encik Abdul Rashid Bin Selamat, Encik Muhammad Khairi Bin Khalid and Encik Mohd Farid Bin Abd. Rahim. Thank you for their help and assistance. Without their precious support, it would not be possible to carry out this research. My sincere thanks also go to postgraduate student, Amirah Binti Hamdi who continuously provided guidance and expertise that has markedly assisted the research.

Last but not least, I am very thankful to my family who have provided me moral support and financial support during final year project period. Their physical and mental supports have encouraged me throughout the project.

TABLE OF CONTENTS

Contents **Page**

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Ar	Argon
C	Carbon
C_2H_4	Ethyne
CH_3COOH	Ethanoic acid
CH_4	Methane
Cl	Chlorine
CO	Carbon monoxide
CO_2	Carbon Dioxide
DSC	Differential scanning calorimetry
EDX	Energy-dispersive X-ray spectroscopy
FCC	Face-centered cubic
GASAR	Gas-metal eutectic solidification
H_2	Hydrogen
HBSS	Hanks' Balanced Salt solution
HCP	Hexagonal close-packed
Mg	Magnesium
$Mg(Cl)_2$	Magnesium chloride
$Mg(OH)_2$	Magnesium hydroxide
MgO	Magnesium oxide
MMA	Methyl methacrylate
PMMA	Poly(methyl methacrylate)
PSA	Particle size analyzer
SBF	Simulated body fluid
SEM	Scanning electron microscope
TGA	Thermogravimetric analysis
W_a	Weight of porous Mg in air
W_b	Weight of porous Mg in water
W_c	Weight of porous Mg after immersed in distilled water.

LIST OF SYMBOLS

%	Percentage
°C	Degree celsius
Wt %	Weight percent
g	Gram
min	Minute
MPa	Megapascal
µm	Micrometer
h	Hour
Vol %	Volume percent
mm	Millimeter
rpm	Rotational per minute
K	Kelvin
ρ	Density

MAGNESIUM BERLIANG MENGGUNAKAN POLI (METIL METAKRILAT) (PMMA) SEBAGAI AGEN PEMBUSAAN UNTUK APLIKASI BIOPERUBATAN

ABSTRAK

Magnesium berliang telah dikenalpasti sebagai logam biodegradasi untuk aplikasi gantian tulang kerana sifat biokompatibiliti yang sangat baik, ketumpatan yang rendah, keupayaan biorosot dalam *vivo* dan sifat-sifat mekanikal yang baik. Dalam kajian ini, magnesium berliang telah difabrikasi melalui metalurgi serbuk menggunakan poli (metil metakrilat) (PMMA) sebagai agen pembusaan. Untuk menentukan suhu optimum pensinteran bagi fabrikasi magnesium berliang, magnesium berliang telah dihasilkan dengan menggunakan proses pensinteran dua tahap pada pelbagai suhu pensinteran (550°C, 585°C dan 620°C) untuk peringkat pertama kajian. Magnesium berliang yang difabrikasi kemudiannya melalui pencirian untuk morfologi, keliangan, ketumpatan, kekuatan mampatan dan EDX. Ketumpatan magnesium berliang bertambah dan keliangan berkurang dengan peningkatan suhu pensinteran. Analisis EDX membuktikan bahawa PMMA terurai sepenuhnya semasa proses pensinteran. Pencirian mekanikal menunjukkan bahawa magnesium berliang disinter pada 620 °C mempamerkan kekuatan mampatan tertinggi dan kepadatan dengan optimum keliangan sebanyak 39.37%. Untuk peringkat kedua kajian, magnesium berliang dengan keliangan sebanyak 39.38 – 40.82% telah dihasilkan dengan PMMA yang berbeza saiz (38-63 μm, 63-90 μm dan 90-125 μm). Kekuatan alah mampatan adalah antara 19.95 MPa dan 23.28 MPa dan bertambah dengan pengurangan saiz zarah PMMA dan keliangan. Secara keseluruhannya, sifat-sifat mekanik Mg berliang adalah dalam julat kekuatan mampatan tulang semula jadi. Keputusan ini membuktikan bahawa PMMA berpotensi untuk digunakan sebagai agen pembusaan dalam magnesium berliang untuk aplikasi bioperubatan.

POROUS MAGNESIUM USING POLYMETHYL METHACRYLATE (PMMA) AS A SPACE HOLDER FOR BIOMEDICAL APPLICATION

ABSTRACT

Porous magnesium has been recognized as a promising biodegradation metal for bone substitute application because of its excellent biocompatibility, low density, ability to biodegrade *in vivo* and excellent mechanical properties. In the present work, porous magnesium was fabricated by powder metallurgy using spherical poly(methyl methacrylate) (PMMA) as a space holder. To determine the optimum sintering temperature for porous magnesium fabrication, the porous magnesium was fabricated using double step sintering process at various sintering temperature (550°C, 585°C and 620°C) in first stage of research. The porous magnesium fabricated was then characterized for morphology, porosity, density, compressive strength and EDX. Density of porous magnesium increases and the porosity decreases with increasing sintering temperature. EDX analysis proved that PMMA was fully decomposed during sintering process. The mechanical characterization indicated that porous magnesium sintered at 620°C exhibited the highest compressive strength and density with optimum range of porosity of 39.37%. For second stage of research, porous magnesium with porosities of 39.38 – 40.82% was produced with different sizes of PMMA particles (38-63 µm, 63-90 µm and 90-125 µm). The compressive yield strength ranges between 19.95 MPa and 23.28 MPa and increases with decreasing PMMA particles size and porosity. Overall, the mechanical properties of porous Mg produced is in the range of compressive strength of natural bone. These results proven that the PMMA has a potential to be used as space holder in porous magnesium for biomedical application.

CHAPTER 1

INTRODUCTION

1.1 Background

Porous materials have gained a significant interest in several high impact sectors such as aerospace, biomedical, automotive, construction and transportation. In fact, porous materials provide a host of extraordinary properties compared to dense solid materials, which includes light weight, good energy absorption, excellent biomimetic properties, low thermal conductivity, high specific strength and stiffness (Liu and Chen, 2014). For instance, porous materials are beneficial in civil engineering design to minimize the weight of structures. Also, porous materials are suitable for bone tissue engineering application as their structure allows adequate spaces for transportation of nutrients and for growth of living tissues.

Generally, artificial porous materials can be categorized further into porous metal, polymer foam and porous ceramics. Each of them have their cons and pro in application. However, only porous metals have gained remarkable attention in orthopaedic applications by researchers. In particular, porous magnesium (Mg) provides tremendous advantages over current orthopaedic implant materials such as bio-ceramics and degradable polymers. These advantages include low density, high damping capacity, ease of machinability, elastic modulus close to that of bone, biocompatibility and ability to biodegrade *in vivo* (Kirkland and Birbilis, 2013). Meanwhile, the porous bioactive ceramics such as hydroxyapatite are also osteoconductive and biodegradable, however, they are very brittle and not suitable for load bearing application (Wen et al., 2004). Also, polymer foam such as polyurethanes and poly(-hydroxyesters) offer controlled biodegradation *in vivo* (Nair and Laurencin, 2007), yet , the mechanical properties of these polymers are often lower than those of human bones. For these reason, biodegradable porous Mg are one of the promising alternative to existing implants.

Fabrication of porous metal materials have been widely developed and studied to tailor their required properties based on application specific features and characteristics. Methods that commonly adopted in fabrication of porous metal includes gas-metal eutectic solidification (GASAR), melt foaming method, melt gas injection, plaster casting and powder metallurgy using space holder technique. However, only a few processes capable of producing open cell structure with no/minimum contaminant in the final product during pattern removal. Among all the fabrication method, powder metallurgy using space holder technique has exhibited the best method for porous Mg fabrication to researcher (Bi et al., 2015, Čapek and Vojtěch, 2013). Powder metallurgy method utilizing space holder materials to produce porous Mg with interconnected pores. In addition, the pores size, pores distribution and porosity of product can be easily modified by controlling the size and shape of starting powders (Čapek and Vojtěch, 2013). Normally, space holder materials will be removed either by thermal decomposition and leaching process. There are variety of space holder material used by current researcher includes sodium chloride (NaCl), carbamide and ammonium bicarbonate.

In general, double step sintering process consists of four main steps, which include mixing process, compaction process, space holder removal process and followed by sintering process. The experimental parameter applied in each process are crucial in deciding the pore morphology, pore distribution, mechanical and physical properties of the resulting product. For instance, Hao et al. (2009) claimed that the compacting pressure should be adequate to break down oxide film at the surface of Mg particles but not so high that that causing space holder materials to deform. In addition, sintering process parameters such as temperature, time, atmosphere also play a very important role in determining final properties of porous Mg. For example, the sintering temperature should not be too low or too high that cause poor inter-particle bonding and partial melting of Mg particle respectively. Meanwhile, Čapek and Vojtěch (2014) proved that it is necessary to consider the sintering condition as it have significant effect on the mechanical properties of porous Mg. Pore size and porosity is another importance aspect to be consider, especially in biomedical application. Porous Mg must have pores size at least 100 µm with interconnected porosity for bone ingrowth (Bose et al., 2012). However, higher porosity and larger pores size may compromise the mechanical properties of the porous metal by enlarging void volume (Murphy et al., 2010).

1.2 Problem Statement

Magnesium has been recognized as a promising biodegradation metal especially for orthopedic applications. Comparing to other biomedical materials they possess several advantages such as light weight, ability to degrade *in vivo* without any harmful effects and have elastic modulus which is closer to that of cortical bone. Currently, fabrication of magnesium with interconnected pores and suitable porosity is possible by using power metallurgy (PM) technique based on space holder particles. For this reason, space holder plays a very importance role in producing porous magnesium with desired porous architecture, mechanical properties and has no adverse effect on the resultant structure.

Previously, Čapek and Vojtěch (2013) synthesized porous magnesium using ammonium bicarbonate as space holder. It was found that the total porosity of materials produced by powder metallurgy using the spacer particles is higher than the sum of the added ammonium bicarbonate. Čapek and Vojtěch (2013) have reported that the expansion of gases (NH_3, H_2O and CO_2) generated in the decomposition of ammonium bicarbonate could contribute to the increased in porosity. In addition, MgO was formed by the reaction of Mg and decomposed space-holding particles that containing oxygen (Bi et al., 2015). It also have been reported that the residue of the decomposed space-holding particles was found in the sintered porous Mg using ammonium bicarbonate (Čapek and Vojtěch, 2014) and carbamide (Zhuang et al., 2008) as space holders. Any reaction between decomposed space-holding particles and magnesium framework may deteriorate the mechanical properties of the resulting scaffolds (Arifvianto and Zhou, 2014). Hence, an alternative space holder materials with very worst affinity with Mg such as poly (methyl methacrylate) (PMMA) was utilised by Bi et al. (2015). Their studies focused on the different percentage of PMMA and the effect of processing parameters such as sintering temperature and space holder sizes on porous structure, mechanical strength and bio-corrosion behavior have not been investigated yet. Sintering temperature are important in determining the mechanical properties of porous magnesium as it governed the bonding between metal matrix particles in porous magnesium (Arifvianto and Zhou, 2014). Moreover, compressibility of porous magnesium are mainly depending on the porosity and pore size (Wen et al., 2004).

In this work, PMMA space holder was used in fabrication of porous magnesium for biomedical purpose with the aim to reduce the undesired reaction between decomposed space-holder particles and magnesium matrix. At the same time, sizes of space holder and sintering parameter such temperature were studied to obtain an optimum parameter for fabrication of porous Mg. The pore morphology, pore size and distribution, total porosity, compressive strength and biocorossion behaviour of sintered porous magnesium were systematically discussed in this research.

1.3 Research Objective

The objectives of this research are:

i. To determine the suitability of poly (methyl methacrylate) as space holder for porous magnesium fabrication.
ii. To evaluate the effect of sintering temperature on the morphology, physical properties and mechanical properties of porous magnesium.
iii. To investigate the effect of space holder sizes on the morphology, mechanical properties, physical properties and degradation behaviour of porous magnesium.

1.4 Thesis Outline

The chapters of this thesis are summarized as follows:

Chapter 1 provides an overview and background of the study, problem statement and objectives of the research.

Chapter 2 covers literature review of works related to porous magnesium. This includes a brief introduction of porous materials and magnesium as biodegradable material, fabrication methods, double sintering process and the properties of porous magnesium.

Chapter 3 describes the research methodology in detail from raw materials preparation to fabrication of porous magnesium, parameters investigated and characterization involved.

Chapter 4 presents a systematic results and discussion of the works which include raw materials characterization and the effect of sintering temperature and size of space holder on the properties of porous magnesium.

Chapter 5 concludes the overall findings of the research and recommendations for future work in porous magnesium fabrication.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Recently magnesium has been identified as a potential material for biomedical application especially in bone tissue engineering. It was used as bone substitute materials because of their good mechanical properties, good biocompatibility and low densities. However, many authors reported that residue of the decomposed space-holding particles has been found in the sintered porous magnesium. Hence, an alternative space holder materials such as Poly (methyl methacrylate) (PMMA) will be used as space holder materials in this study. Moreover, the effect of sintering temperature and space holder sizes on the porous structure and mechanical strength will be systematically discussed in this research.

2.2 Porous Materials

Porous materials are defined as solids containing pores. Porous solid are made of a continuously solid phase that forms the basic porous frame and a fluid phase that forms the pores in the solid (Liu and Chen, 2014). Porous materials play a very importance role in many aspects of daily necessities such as water purification by activated carbon or advance application such as porous electrode in fuel cell and heat radiators in aircraft, high speed trains and microelectronics. Porous solids often serves as structural bodies in nature, including in wood and bones (Gibson et al., 2010). In addition, porous materials are significance for biomedical applications as their structure allows adequate spaces for transportation of nutrients and for growth of living tissues (Gupta and Meenashisundaram, 2015). However, nowadays, human being utilise porous materials more functionally than structurally, and invent many structural and functional integrative application fully used these materials.

Generally, pores are classified in two types, open pores and closed pores as illustrate in Figure 2.1. Open pores are pore that connect to the outside of the material whereas closed pores are isolated from the outside and may contain a fluid. For most industrial applications of porous materials, high fraction of open porosity is required for filters and carriers for catalysts and bioreactors application, whereas, closed porous materials are used mainly for sonic and thermal insulators, or low-specific-gravity structural components. In general, artificial porous materials can be classified further into porous metal, polymer foams and porous ceramics. Each of them have their own pro and cons in certain application, but all the types have some identical characteristics, including low relative density, high specific strength, large specific surface area, small thermal conductivity and good energy absorption compared to dense version of the original materials (Liu and Chen, 2014).

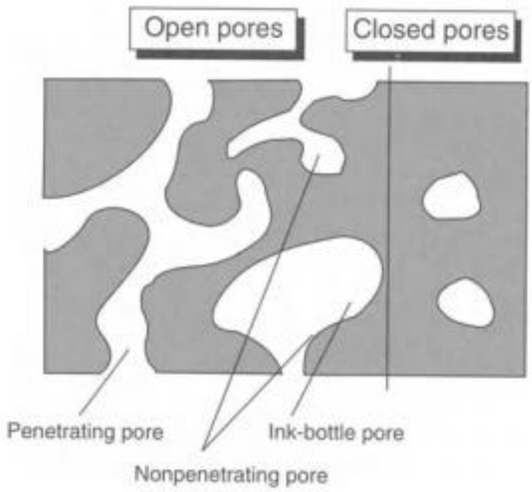

Figure 2.1: Schematic illustration of different morphology of pores (Ishizaki et al., 2013)

2.2.1 Porous Metal

Porous metals are relatively a new class of engineering material that possess good functional and structural properties. Compared to dense solid metal, porous metal offers a host of extraordinary properties, including light weight, good energy absorption, large specific area and high specific strength and stiffness. Some porous metal can be produced with predefined properties, relying on the required application, by varying material and internal structure (Dukhan, 2013). Therefore, they are widely used in aerospace, transportation, medical, environmental protection, metallurgy, construction, electrochemistry and bioengineering industries. For instance, porous aluminum are used to reduce the weight of vehicles and can make up the light and heat-transferring supporting in aircraft and missiles and also reinforcement parts in the load-bearing structures of satellites (Liu and Chen, 2014). In addition, some porous metal (magnesium and titanium) are used as bone replacement materials with controllable pore size and porosity (Wen, 2016).

Many studies have recently been carried out on porous metals/metallic foams. For instance, Nieh et al. (2000) studied the effect of cell morphology on the compressive properties of open-cell aluminum foams and it was found that cell size appears to have a negligible effect on the strength of foams, at a fixed density, the cell shape was shown to effect the strength of foams. Kashef et al. (2011) investigated fatigue crack growth behavior of titanium foams for biomedical applications. Other than that, porous metal foams include copper, bronze, iron, steel, silver, gold, zirconium, tantalum and magnesium have receiving a lot of attention from researchers. However, porous magnesium has attracted more attention in the field of biomedical applications for its remarkable biocompatible and biodegradable advantage (Bi et al., 2015).

2.2.2 Magnesium

Magnesium (Mg) is the eighth most abundant element in earth's crust by mass. Magnesium was first discovered by a Scotish chemisy, Joseph Black in 1755. However, he was unable to isolate this element until 1808 by a chemist and scientist Sir Humphrey Davy. Davy successfully isolate magnesium by decomposed the wet magnesium sulphate by electrolysis using a voltaic cell and a mercury cathode (Friedrich and Mordike, 2006). Mg can be found in different ores like dolomite, magnesite, brucite, carnallite, tal and olive.

In general, Mg is a chemical element in the alkaline earth metal group with atomic number 12 and common oxidation number +2. Mg has a hexagonal close-packed (HCP) structure and it's not as ductile as the face centered cubic (FCC) metals such as aluminum and silver. Mechanical properties and physical properties of Mg are as shown in Table 2.1. Since its discovery, Mg has been developed and used extensively in various applications from automotive appliances, aircraft, and electronic devices to biomedical applications. Magnesium is getting a lot of attention lately due to its excellent properties such as lightweight, considerable mechanical and biodegradable properties.

Table 2.1: Physical and mechanical properties of Magnesium (Kirkland et al., 2011)

Physical Property	Value	Mechanical Property	Value
Melting Point	650 ± 2°C	**Tensile Strength**	90-220 MPa
Boiling Point	1107 ± 10°C	**Compressive Yield Strength**	21-115 MPa
Heat of Combustion	25.1 MJ/kg	**Elongation**	2-15 %
Specific Heat (At 20 °C)	1030 J/(kg K)	**Young's modulus**	41-45 GPa
Thermal Conductivity at 25 °C	155 W/(kg K)	**Specific strength**	158 kN×m/kg

2.2.3 Porous Magnesium

In recent years, as a kind of obligatory element to human body, magnesium (Mg) are getting popular in bone tissue engineering applications, especially in load-bearing applications. At the same time, stainless steel (Rondelli et al., 2005), titanium (Zhang et al., 2015) and cobalt–chromium alloys (Pham et al., 2013) are also widely used for orthopaedic applications, particularly for bone fracture implants. However, secondary surgery may be necessary after implantation of those metallic materials because of removal of implant after healing and adverse effects such as implant intolerance or loosening during prolonged healing (Kang et al., 2016). Moreover, porous bioactive ceramic (Hench and Jones, 2015) and polymeric foam (Rezwan et al., 2006) have also been developed for tissue engineering bone and cartilage. Nevertheless, the porous bioactive ceramic and polymeric scaffold materials exhibit poor mechanical properties. For instance, the porous bioactive ceramics are very brittle, whereas the strength and Young's modulus of the porous polymers are often lower than those of human bones. As a substitute, biodegradable material with sufficient mechanical stability, good biocompatibility and light weight such as porous Mg have been extensively researched in recent years.

Wen et al. (2004) investigated effects of the porosity and pore size compressibility of porous Mg. Carbamide particles with varied sizes; 45–100; 100–200; 200–300; 300–500 µm were used as space holder particles. Results indicated that the Young's modulus and peak stress increases with decreasing porosity and pore size, however, the mechanical properties of the porous Mg were in a range of those of cancellous bone.

In addition, Čapek and Vojtěch (2013) have synthesized porous Mg using magnesium powder (75-150 µm) and ammonium bicarbonate (250-500 µm) as space holder. The results indicated that the flexural strength of porous Mg with porosities up to 28 vol.% is greater than that of common implantable porous materials, such as porous hydroxyapatite or porous composite bioglass. The mechanical properties of the synthesized porous Mg were also comparable to that of natural bone. Meanwhile, Čapek and Vojtěch (2014) studied the effect of sintering conditions on the microstructural and mechanical properties of porous magnesium. They concluded that for sintering up to 6 h, the effect of atmosphere purity on sample microstructure or mechanical behavior was not significant. However, for sintering time more than 6 h, the purity of the argon atmosphere affects the mechanical properties of porous Mg. Also, the result indicated that the sintered porous Mg possess mechanical properties similar to those of natural bone tissue.

2.2.4 Magnesium as Biomaterial

Mg and its alloys offer a number of other benefits over many current implant materials, including low density, high damping capacity, ease of machinability, elastic modulus close to that of bone, biocompatibility, ability to biodegrade *in vivo* and osteogenicity (Kirkland and Birbilis, 2013). Moreover, magnesium is the second most abundant intracellular cation and, on the whole, the fourth most abundant cation in the body. The normal adult contains about 22–24 g of magnesium and about 60% of the magnesium is present in the bones, of which 30% is exchangeable and functions as reservoir to stabilize serum concentration (Watson et al., 2012). About 20% is in skeletal muscles and 19% in other soft tissues. Hence, magnesium is essential to human metabolism and the excess of Mg can be removed via urinary system. Furthermore, magnesium may actually have stimulatory effects on the growth of new bone tissue and remain present in the body and maintain mechanical integrity over a time scale of 12–18 weeks while the bone tissue heals, eventually being replaced by natural tissue (Staiger et al., 2006).

Furthermore, density of Mg is almost identical to that of natural bone, which range from 1.8–2.1 g/cm^3 (Staiger et al., 2006). For that reason, porous implant (also known as scaffold) made from Mg will not bring in significant weight increase as compared to other metallic biomaterials such as aluminium, titanium and stainless steel. From Figure 2.2., it is clearly showed that Mg exhibit mechanical properties that close to that of native bone and it has higher potential to minimize the rise of stress shielding that can lead to bone loss around the implant (Zhou et al., 2015). Excellent biodegradability in Mg also make it an ideal alternative material for orthopaedic applications (Gupta and Meenashisundaram, 2015). Mg capable of performing a temporary function *in vivo* and be completely replaced by new tissue growth overtime. Hence, it reduces the need for secondary surgery that will increasing health care costs, and patient discomfort.

Table 2.2: Summary of the mechanical properties of porous biomaterials in comparison to natural bone (Čapek and Vojtěch, 2014)

Material	Porosity (vol.%)	Pore size (μm)	UFS (MPa)	CYS (MPa)	UCS (MPa)	Reference
Natural bone	–	–	2–150	–	2–180	[13]
Porous Mg	29–31	250–500	3–15	13–53	20–70	This study
Porous Mg	23–38	250–500	4–17	–	–	[19]
Porous Mg	14–44	250–500	2–5	–	–	[22]
Porous Mg	36–55	200–400	14–27	–	15–31	[13]
Porous Mg	52–70	~1250	–	–	4–14	[8]
Porous Mg	50	200–500	–	–	2	[14]
Porous Mg	28	170	–	–	24	[7]
Porous Mg	35–55	100–400	–	–	12–17	[11]
Porous Ti	78	200–500	–	–	35	[14]
Porous hydroxyapatite	50–77	200–400	2–7	–	1–17	[13]
Porous hydroxyapatite	–	366–444	–	–	30	[25]
Porous composite (poly-L-lactide + 20–50 wt.% of bioglass)	77–88	~100	1–4	–	~0.4	[13]
Porous polycaprolactone	48–77	–	–	2–3	–	[25]
Porous polycaprolactone	37–55	–	–	–	2–3	[25]
Porous polycaprolactone	55–56	–		2–3		[26]
Porous polylactide-co-glycolide	31	116	–	–	0.5	[27]
Porous composite of polylactide-co-glycolide and 45S5 bioglass	43	89	–	–	0.4	[27]

2.2.5 Requirement of Magnesium as Porous Scaffold

Scaffold materials for bone tissue engineering must meets certain criteria to achieve both nutritional and biological needs for the specific cell population involved in tissue formation. Common properties of scaffold that must acquire include high biocompatibility, biodegradability and mechanical compatibility, and the scaffold must possess substantial strength to match host bone properties. Furthermore, an ideal scaffold needs to form blood vessels in or around the implant within few weeks of implantation to actively support nutrient, oxygen, and waste transport (Bose et al., 2012).

Moreover, it is known that one of the critical factors for bone ingrowth is the size of interconnecting pores. An interconnected porous structure permits the transport of body fluids to damage or wound tissue and supports the incorporation of new tissue in the implant. Rouwkema et al. (2008) claimed that scaffolds must be interconnected porosity with a minimum pore size of 100 μm in diameter for successful diffusion of essential nutrients and oxygen for cell. However, Itälä et al. (2001) also showed the formation of an osteonal bone structure in pore sizes as small as 50 mm was possible under non load bearing condition. According to Bose et al. (2012), pore sizes in the range of 200–350 mm is found to be ideal for bone tissue in-growth. They also revealed that scaffold must have good bioresorbability so that the porous scaffold able to degrade with time *in vivo*, preferably at a controlled resorption rate and eventually creating space for the new bone tissue to grow.

2.3 Fabrication of Porous Magnesium

In recent time, porous Mg materials and their preparation methods have been extensively developed and studied owing to the advantages of magnesium as a biomaterial. Researchers had shown that porous magnesium could be synthesized using melt foaming method (Yang et al., 2010), melt gas injection (Staiger et al., 2006), gas-metal eutectic solidification (GASAR) (Gu et al., 2010) , plaster casting (Gu et al., 2010) and powder metallurgy using space holder technique (Yilong et al., 2016, Bi et al., 2015, Cay et al., 2013).

2.3.1 Metal Gas Injection

Fabrication of porous metals can be accomplished by simply injecting gases (air, nitrogen and argon) into the molten metal or metallic melt. However, gas bubbles formed in the melt normally will quickly rise to its surface due to high buoyancy forces in the high-density liquid. To retain the bubbles in the melt, stabilizing particles such as fine ceramic powders or alloying elements must added to the metallic melt to enhance the viscosity. After that, the melt is foamed by introduced gases into it using a rotating impellers or vibrating nozzles. These generate very fine and distributed gas bubbles in the melt. Finally, molten metal was pulled off the liquid surface with a conveyor belt and is then allowed to cool down and solidy. The schematic diagram of metal gas injection method is shown in Figure 2.3. Staiger et al. (2006) have reported that porous magnesium metal implant can be successfully fabricated using argon gas injection to molten magnesium. However, production using foaming by injection of argon gas to the molten metal did not fabricate a product with consistent morphology/pore shapes and this approach has been abandoned.

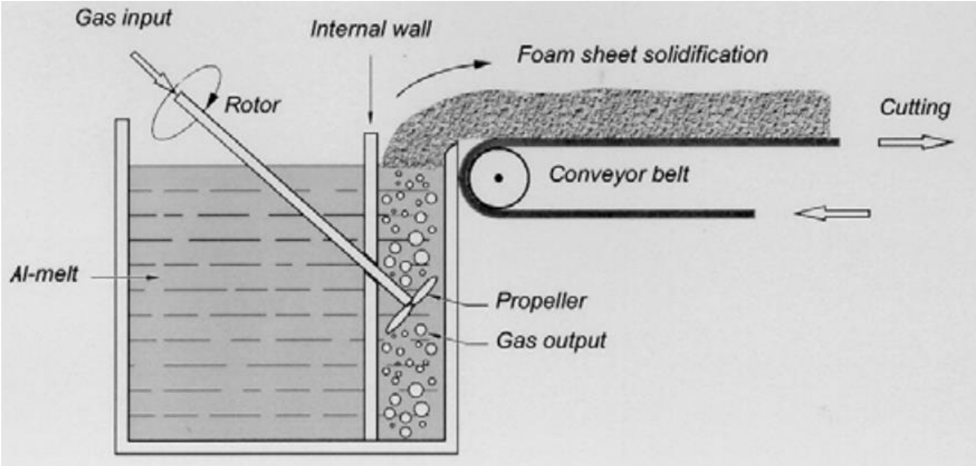

Figure 2.3: Direct foaming of melts by gas injection (Banhart, 2001)

2.3.2 Melt Foaming Method

Melt foaming method is one of cost-effective methods to make porous metals. This method utilizing a blowing agent to produce cellular metal foams with close pore structures. Under the influence of heat and releases gas, the blowing agent will be decomposed which then initiates the foaming process. For instance, Yang et al. (2008) employed this method to fabricate porous magnesium foam. Calcium carbonate ($CaCO_3$) was used as blowing agent in the research. Firstly, a define quantity of Mg (1kg) was melted in a crucible at fixed temperature and then granular calcium (2 wt%) introduced into the melted Mg by the impeller with a constant revolution speed of 400 rpm for 10 min to enhance viscosity of melted Mg. The thickened Mg melt was then foamed by adding the blowing agent, $CaCO_3$ powder (2.0 wt.%). During the fabrication process, the melt was held in the furnace to let bubbles in the melt continuously grow until a certain cellular structure is formed., the stirring foaming time and holding foaming time were both set as 30 s. The fabrication process was performed under the mixed gas atmosphere of CO_2 and SF_6 (volume ratio: 6:1) to prevent the melt from ignition. Unfortunately, size, shape and location of pores within the matrix varies, relying on the parameters of the fabrication process. In addition, limited porosity and variations in pore size and shape are often observed in the result of porous material (Ryan et al., 2006). Schematic diagram of apparatus for making Mg/Mg alloy foams using foaming agent was illustrated in Figure 2.4.

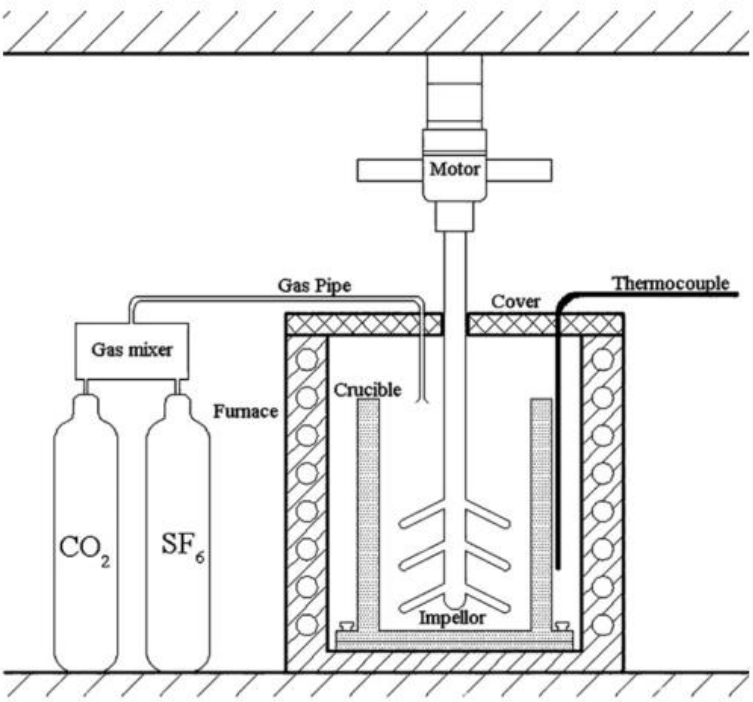

Figure 2.4:Schematic diagram of apparatus for making Mg/Mg alloy foams using foaming agent (Yang et al., 2008)

2.3.3 Gas-Metal Eutectic Solidification (Gasar Process)

Many metal alloy-hydrogen binary phase diagram shows a eutectic system. These include Al, Be, Cr, Cu, Fe, Mg, Mn and Ni-based alloys (Ashby, 2000). Gas-metal eutectic solidification type of porous metal foam is formed by dissolving hydrogen gas in molten metal releasing during direction cooling. During solidification, porous material containing hydrogen-filled pores are formed when metal and hydrogen simultaneously form by a gas eutectic reaction. The resultant product often called as lotus-type porous metal or porous metals with directional pores due to it similar structure to plant lotus roots.

SEM morphologies of cross section and longitudinal section of porous pure magnesium fabricated by Gu et al. (2010) using GASAR method is displayed in Figure 2.6.

Čapek and Vojtěch (2014) and Gupta and Meenashisundaram (2015) have reported that open-cell structures are difficult to be achieved by GASAR technique In addition, Ashby (2000) reported that GASAR method have certain safety issues and costly. Hence, they remain confined to the laboratory and are not yet commercially available in market.

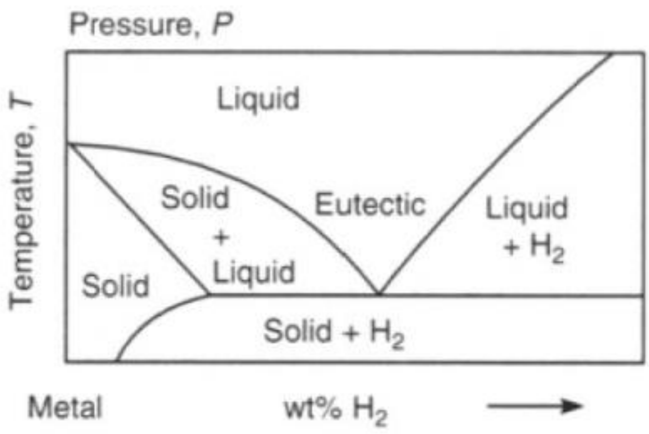

Figure 2.5: Metal-hydrogen binary phase diagram (Ashby, 2000)

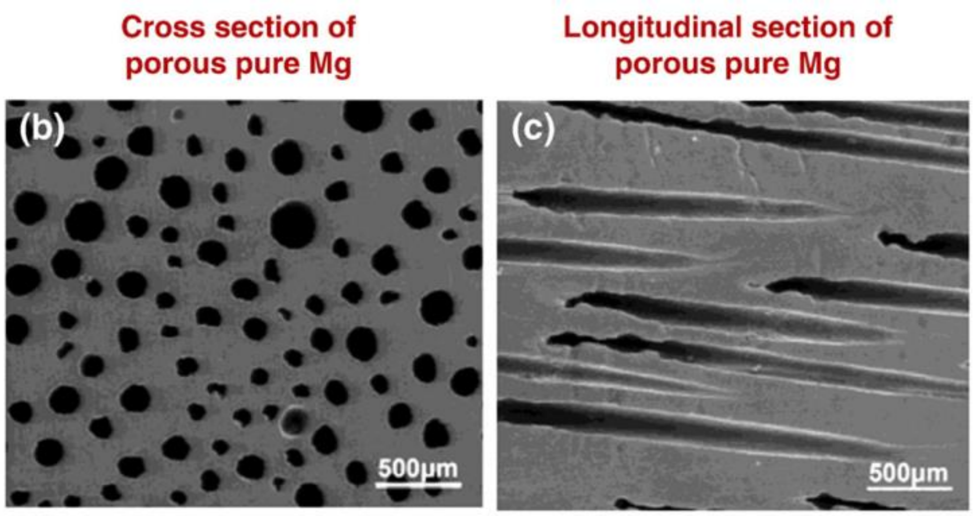

Figure 2.6: SEM morphologies of cross section and longitudinal section of porous pure Mg (Gu et al., 2010)

2.3.4 Plaster Casting

Plaster casting is a method to fabricate porous metals by utilizing an open cell polymer foam mold template with the predefined cell size and relative density. For example, Yamada et al. (2000) fabricated open-cellular AZ91 magnesium (Mg) using polyurethane foam as shown in Figure 2.7 . Firstly, plaster was poured into a polyurethane foam, and then the plaster mold was heated to 773k to remove the polyurethane foam and formed plaster mold with porous structure. After that, molten Mg was then introduced into the porous plaster mold heated to 873K. Finally, the mold was evacuated and the plaster mold was broken down by the water spray to obtain open-cellular magnesium. The result shown that this method able to produce cellular magnesium or porous magnesium with density as low as 0.05 g/cm^3 and the cellular has a high potential as energy absorber. However, issues about contamination and corrosion of the final product may occur during pattern removal had been reported by Čapek and Vojtěch (2014) and Gupta and Meenashisundaram (2015).

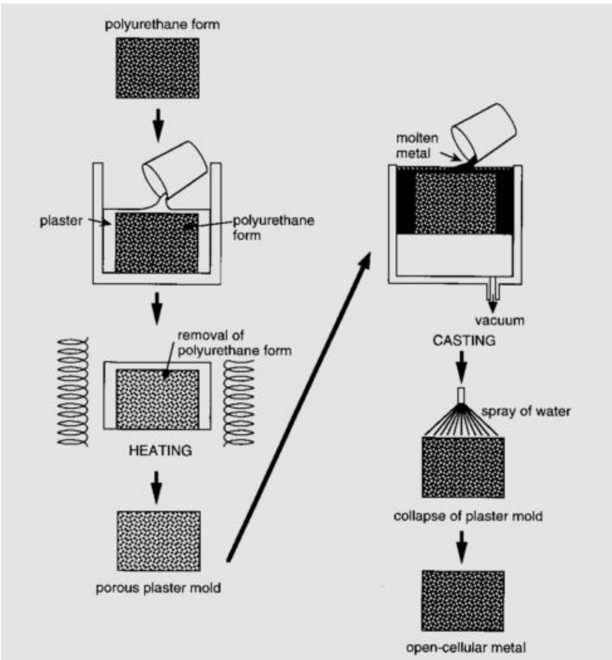

Figure 2.7: Schematic illustration of production of an open-cellular Mg foam using plaster casting method (Yamada et al., 2000)

2.3.5 Powder Metallurgy Using Space Holder Technique

Powder metallurgy is a promising technique that utilised space-holder particles to allow the fabrication of porous materials with interconnected pores. The mechanical properties of the material can be modified by changing the pore size and distribution. This can be done by controlling the size and shape of the powder grains in the starting material and by selection of the sample preparation conditions such as sintering time, temperature and compacting pressure (Hao et al., 2009). In general, fabrication route of porous metals with the space holder method consist of four stages, including mixing, pressing, space holder removal process and sintering as shown in Figure 2.8. Firstly, the space holder material that act as pore former are mixed and compacted together with metallic matrix powder. After that, the space holder particles are removed either before or during sintering, forming new pores behind in the metal matrix.

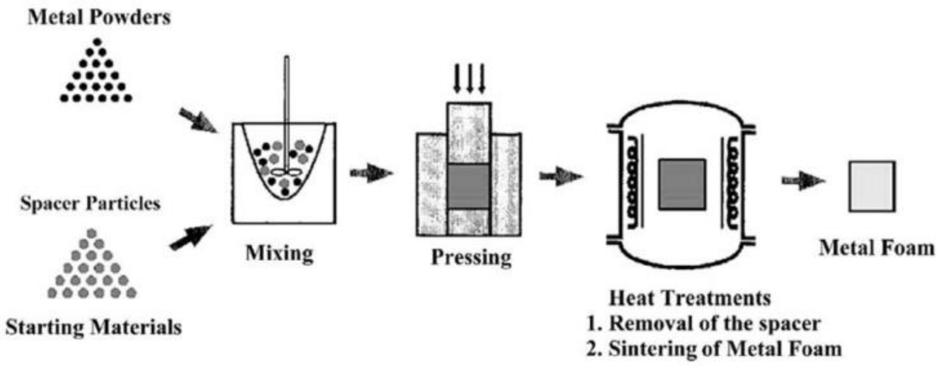

Figure 2.8: Schematic illustration of fabrication route of metallic foam with the space holder method (Arifvianto and Zhou, 2014)

For instance, Čapek and Vojtěch (2013) studied the properties of porous magnesium (Mg) prepared by powder metallurgy. Mg powder (75-150 µm) was used as the parent material and an ammonium bicarbonate powder (250-500 µm) was used as space holding material. Different amount of ammonium bicarbonate (0, 5, 10, 15, and 20 vol.%) was used of and liquid hexane (30 vol.%) was added as binder to avoid segregation of powders. The mixture was compacted under uniaxial pressure of 265 MPa to form green compact and then heat-treated using double sintering process at 130 °C for 4 h followed by 550 °C for 6 h. The double sintering process for fabrication Mg porous also was demonstrated by other researchers (Bi et al., 2015, Kowalski and Jurczyk, 2015, Cay et al., 2013, Hao et al., 2009). This showed that double sintering process in the best way to fabricate porous Mg using space holder method.

Besides, selection of space holding material is very crucial in this method. This is because any reaction between decomposed space holding particles and metal matrix may deteriorate the mechanical properties of the resulting product (Kim et al., 2013). To minimize the negative effects on the resultant product due to contamination by the residues of space-holding particles, variety of space holders had been used by most of researchers to produce porous magnesium. This include sodium chloride (Kang et al., 2013), ammonium bicarbonate (Čapek and Vojtěch, 2013, Kowalski and Jurczyk, 2015), carbamide (Wen et al., 2001, Zhuang et al., 2008) and Poly(methyl methacrylate) (Bi et al., 2015). In this work, PMMA is choose as space holder due to it very worse affinity with Mg as compared to ammonium bicarbonate and carbamide (Bi et al., 2015).

2.4 Double Sintering Process

Double sintering process has been frequently used in fabrication of porous magnesium as discussed in Chapter 2.4.5. In general, double sintering process consist of four main steps, which include mixing process, compaction process, space holder removal process and sintering process. Parameters of each process in double sintering process must be select with care as it will significantly affect the properties of end products.

2.4.1 Mixing Process

Mixing of matrix powder and space-holder material is carried out as the first step in porous magnesium fabrication. The aim of mixing process is to combine two or more dissimilar materials to obtain a homogeneous product. Improper mixing or low mixing efficiency can cause porosity levels of end products deviate from the designated values (Arifvianto and Zhou, 2014). Meanwhile, Čapek and Vojtěch (2013) discovered that the total porosity of materials prepared by powder metallurgy using the spacer particle is higher than the sum of the added ammonium bicarbonate. The difference is approximately 6 vol.% for all the prepared materials. In addition, powder agglomeration and adhesion of mixed powder particles to the inner surface of the mixing container wall may also due to low mixing efficiency. Consequently, the resulting mixture is less uniform because of inhomogeneous distribution of space holder particles.

Besides, powder segregation is often occurring during the mixing process due to difference in size and density between powder components. This problem can be minimized by using suitable binder. Binders will help to produce a sufficient binding strength between metal matrix powder and space-holding particles and yet not be reactive to both powders. At present, several binder have been used for the fabrication of porous magnesium, including ethanol (Kang et al., 2016, Yilong et al., 2016), hexane (Čapek and Vojtěch, 2014) and paraffin (Hao et al., 2009). In this work, a small amount of ethanol (2% in weight) was added during the mixing process to avoid segregation of magnesium and Poly (methyl methacrylate) (PMMA) powders. Mg powder and PMMA were mixed in polyethylene bottle for 1 hour utilizing alumina ball as milling media with weight ratio of powder to ball was 1:10.

2.4.2 Compaction Process

Compaction is a process by which a powder is introduced into a die to make a powder compact by pressing. The purpose of compaction is to obtain a certain green strength that can keep the mixture of powders intact. During compaction, powder particles rearrange themselves, fill the void between the interstices of loose powder particles and increase packing coordination (Arifvianto and Zhou, 2014). Moreover, the number of contact points and the contact area of powder particles increase as the compacting pressure increases, leading to densification of green compact. Hao et al. (2009) reported that the aim of compacting is not only to form green compact, but also to disrupt the oxide film at the surface of the metallic powder. The fracture of oxide film by compaction occurs may due to large shear strains, stress concentrations, scratching and jabbing that occur when metallic powder and space holding particles are pressed against one another during the rearrangement of the particles under a given compacting pressure. Hence, powder compaction enhances the sinterability of metallic powder as direct contact of compacted powder particles can be achieved when there is no oxide film on the powder particle surface.

Hao et al. (2009) and Čapek and Vojtěch (2013) suggested the optimum compacting pressures of magnesium should be in between 200 and 300 MPa. If the compaction pressure is lower than 150 MPa, it is difficult to disrupt the oxide film at the surface on the Mg particles. However, if the compaction pressure more than 300 MPa, green compact will be crumble and disperse in the subsequent dissolution stage and cause undesirable deformation of the pores in the final products.

2.4.3 Space Holder Removal Process Through Heat Treatment

After compaction process, the space holder materials need to be removed either by heat treatment or leaching, depending on the nature of the materials. For heat treatment process, removal of space holder only occurs at temperature higher than decomposition temperature of the specific space holder materials. At the removal temperature, thermal decomposition and evaporation of space-holding material occurs. The space holder will evaporate and escape from the green compact along with inert or flushing gas that leaves the furnaces (Arifvianto and Zhou, 2014). Table 2 shows decomposition and removal temperature of several space holders that commonly used.

Table 2.2: Decomposition and removal temperature of space holders

Space holder material	**Decomposition temperature (°C)**	**Removal temperature (°C)**	**References**
Ammonium bicarbonate	36-70	130	(Čapek and Vojtěch, 2014)
Carbamide	133	>600	(Dizlek et al., 2009)
Polymethyl methacrylate	260	400	(Bi et al., 2015)

Thermogravimetric analysis (TGA) is always the best characterization method to identify the decomposition and removal temperature of a space holder materials. Figure 2.9 below demonstrate the results acquired from TGA, exhibiting weight loss due to thermal decomposition of Poly(methyl methacrylate) (PMMA) that was used as the space holder in the study of Bi et al. (2015). TGA curve indicated that thermal decomposition of PMMA started at around 260°C and finished at 400°C. PMMA will be decomposed into low-molecular-weight stable species (H_2, CO, CO_2, CH_4, C_2H_4, CH_3COOH) in trace amounts.

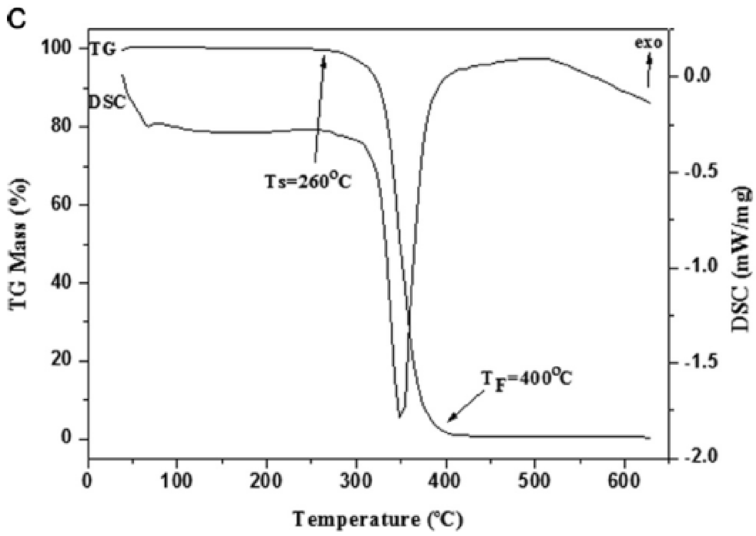

Figure 2.9: DSC and TG curves of Polymethyl methacrylate (Bi et al., 2015)

2.4.4 Sintering

Sintering is a process by which a powder compact is transformed to a strongly bonded monolithic mass with the removal of inter-particulate pores. Sintering is usually performed at elevated temperature where bonding between metal matrix particles in green compact occurs. A normal powder sintering process consist of three stages as shown in study of Wang et al. (2009). At stage 1, growth of sintering bond from original loose powder take places at powder particle contact point and sintering neck are forms. As sintering proceed to stage 2, voids/pores at powder particle interstices are rounded, along with densification and grain growth that occur simultaneously. At last stage, powder densification become less predominant and occur at slower rate than the earlier stages of densification process. Sintering process parameters such as sintering time and temperature must be chosen properly as it will affect the densification and mechanical properties of resulting metallic foam. For instance, incomplete sintering will lead to the formation of micro pores, reduce the load-bearing cross-sectional area of cell wall and consequently deteriorate the compressive strength of scaffolds (Kotan and Bor, 2007).