MECHANICAL PROPERTIES OF POROUS NITI SHAPE MEMORY ALLOY

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DECLARATION

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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This thesis is the result of my own investigations, except where otherwise stated.

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LIST OF ABBREVIATIONS

%	Percent
µm	Microo meter
Å	Angstrom
Af	Austenite-finish-temperature
Al	Aluminium
AM	Additive Manufacturing
As	Austenite-start-temperature
at%	Atomic percent
AuCd	Cadmium-gold
℃	Degree Celsius
CaH2	Calcium Hydride
Cr	Chromium
Cu	Copper
DSC	Diffraction Scanning Calorimeter
EIGA	Electrode Induction-melting Gas Atomization
Fe	Iron
GPa	Giga Pascal
kN	Kilo Newton
LPBF	Laser Powder Bed Fusion
Matr.	Matrix
Mf	Martensite-finish temperature
mm	millimeter
MPa	Mega Pascal
Ms	Martensite-start temperature
NaCl	Sodium Chloride
Nb	Niobium
Ni	Nickel
Ni3Ti	Nickel—Titanium (3/1)
NiTi	Nickel Titanium
NiTi2	Nickel—Titanium (1/2)
O	Oxygen
SE	Superelasticity
SEM	Scanning Electron Microscope
SHS	Self-propagating High-temperature Synthesis
SLM	Selective Laser Melting
SMA	Shape Memory Alloy
SME	Shape Memory Effect
syn	Synthetic
THP	Thermohydrogen Process
Ti2Ni	Titanium Nickel
TiH2	Titanium Dihydride
UTM)	Universal Testing Machine
vol%	Volume percent
wt%	Weight percent
XRD	X-Ray Diffraction
α	Alpha

θ	Theta
ρ	Density

ABSTRAK

Aloi ingatan bentuk (SMA) adalah salah satu jenis aloi yang sangat unik kerana keupayaannya untuk kembali kepada bentuk asal. SMA boleh mengingati bentuk atau corak selepas aloi mengalami ubah bentuk plastik. Walaupun aloi mengalami rangsangan yang menyebabkan aloi berubah bentuk, ia akan kembali semula kepada bentuk atau corak selepas rangsangan tamat. Fenomena ini dikenali sebagai kesan ingatan bentuk (SME). Banyak kajian mendapati bahawa SMA NiTi menunjukkan utiliti yang hebat dalam bidang bioperubatan dan ia boleh digunakan pada implantasi. Walau bagaimanapun, terdapat masalah bahawa bahan semasa mungkin mempunyai ketidakpadanan dalam modulus elastik antara tulang manusia dan bahan logam yang menyebabkan perisai tekanan berlaku dan membawa kepada penyerapan tulang. Penyelesaian untuk masalah ini untuk membuat struktur berliang di dalam bahan untuk meningkatkan kekuatannya. Oleh itu, kesan agen pembentuk liang, CaH_2 terhadap sifat mekanikal NiTi SMA berliang yang difabrikasi menggunakan kaedah metalurgi serbuk dengan penambahan peratusan berat CaH_2 yang berbeza. Sampel kemudian menjalani ujian pencirian dan mampatan untuk menganalisis sifat sampel. Keputusan menunjukkan bahawa peningkatan peratusan berat CaH_2 meningkatkan saiz liang dalam sampel dan juga mengurangkan ketumpatan sampel dan meningkatkan keliangannya. Peningkatan dalam CaH_2 juga akan menjejaskan suhu transformasi austenit dan martensit dan perubahan entalpi tindak balas. Tegasan mampatan dan Modulus Muda berkurangan apabila CaH_2 bertambah dalam sampel. Dalam aspek aplikasi bioperubatan, tegasan mampatan dan Modulus Young yang direkodkan dalam semua sampel boleh memenuhi permintaan untuk implantasi bioperubatan kerana sampel berpuas hati dalam julat nilai rujukan tulang manusia seperti tulang cancellous dan kortikal.

ABSTRACT

Shape memory Alloy (SMA) is one type of alloy that is very unique for its ability on returning to initial shape. SMA can remember the shape or pattern after the alloy undergo plastic deformation. Even if the alloy experience the stimuli that made the alloy to change its shape, it will return back to the shape or pattern after the stimuli ends. These phenomenon is known as shape memory effect (SME). Many studies found that NiTi SMA shows a great utility in biomedical field and it can be used on implantation. However, there is a problem that the current material may have mismatch in elastic modulus between the human bone and metallic material which causes stress shielding to occur and leads to bone resorption. The solution for this problem to make porous structure inside the material to improve its strength. Hence, the effect of pore forming agent, CaH_2 on the mechanical properties of porous NiTi SMA fabricated using powder metallurgy method with the addition of different weight percentage of CaH_2. The samples then undergo characterization and compression testing to analyse the samples' properties. Result show that the increasing of weight percentage of CaH_2 increase the pore size in sample and also decrease the sample density while increase its porosity. Increasing in CaH_2 will also affect the austenite and martensite transformation temperatures and enthalpy changes of reactions. The compressive stress and Young Modulus decreases as the CaH_2 increases in samples. In the aspect of biomedical application, the compressive stress and Young's Modulus recorded in all samples can meet the demand for biomedical implantation as the samples satisfied within the range of the reference value of human bones like cancellous and cortical bone.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Shape Memory Alloy (SMA) or ‘smart alloy’ is a unique metallic alloy which has the ability to return to its initial shape when the alloy undergoes high temperature. This kind of alloy behaves like it can remember its shape or pattern after it undergoes plastic deformation, but when the alloy immersed inside hot water, it will return back to its original shape and when it is away from hot water, the alloy will transform into that shape again. The existence of SMA was first discovered by Arne Ölander in 1932[1], says that the shape memory material was discovered inside the cadmium-gold (AuCd) alloy. The term ‘shape memory’ was first introduced and described by a researcher called Vernom in 1941[2]. At the beginning, the shape memory effect did not show much important to the world. Researchers then was found that the happening of the shape memory was because of the reversible martensitic transformation[3]. The discovery of this reversible reaction brings a very significant attention among the material scientists at that time. However, only few types of alloy include AuCd exhibits such shape memory behaviour until William Buchler and Federick Wang found out the shape memory effect (SME) inside a nickel-titanium (NiTi) alloy in 1962[4]. Since then, the presence of shape memory alloy starts to spread widely and get a huge attention from the community. The demand of the shape memory alloy was increasing due to the application in the technical and also engineering field. Later research was found that with the addition of theird element inside the shape memory alloy such as Iron (Fe) or Niobium (Nb) can change its material properties. Further study also shows that the microstructure, manufacturing procedure and heat treatment could affect the behaviour of shape memory alloy significantly[3]. Researches and studies on the SMA revealed

that the strain inside the SMA can be recovered at room temperature automatically. This phenomenon can be called superelasticity (SE) or pseudoelasticity.

The shape memory alloy has two dominant phases which are martensite and austenite, with three different crystal structure like twinned martensite, detwinned martensite and austenite. The martensite was stable at low temperature while austenite was stable in high temperature. These two different crystal structures can have related to the orientation variants of the martensite crystal. The phase transition from austenite to martensite is known as forward transformation while the phase transition from martensite to austenite is called reverse transformation. When a SMA is heated, it transforms from martensite to austenite phase. The austenite-start-temperature (A_s) is the temperature where the transformation starts and the austenite-finish-temperature (A_f) is the temperature where the transformation is finish. As the SMA is heated beyond the A_s, it start to contract and transform into the austenite structure[5]. During cooling process, the transformation reverts to the martensite at martensite-start temperature (M_s) and finish when it reaches the martensite-finish temperature (M_f)[4]. SMA which goes beyond the highest temperature will permanently deformed. The visualisation of the phase transformation can refer to the figure 1.1.

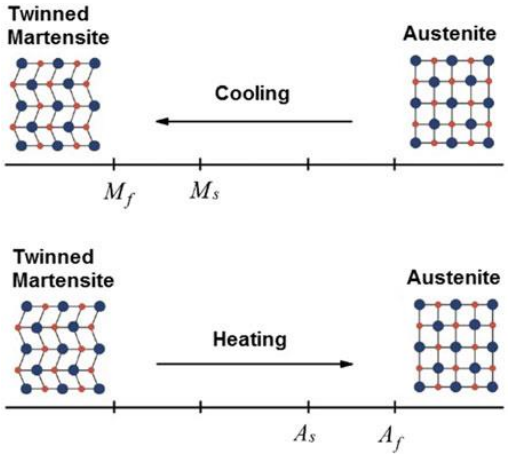

Figure 1.1 Phase transformation of shape memory alloy without any mechanical loading.[3]

Among the various type of shape memory alloys, NiTi-based alloy is the outstanding one not only because of its SME and the pseudoelasticity, the NiTi-based alloy is also a good material in resistance to corrosion and fatigue. Recent studies show that porous NiTi shape memory alloy has attracted the attention for its possibility or potential in medical implant devices and also as a high energy absorption structural material. This kind of alloy not only exhibit the shape memory effect, it also has other properties such as excellent corrosion resistant, wear resistance, mechanical properties and good biocompatibility[6]. Hence, porous NiTi SMA has start to become one of the important material that will be used in the biomedical application, such as stents, heart valve tools, bone anchors, implants etc. It contains cellular structure which was similar to natural material such as bone that is suitable to mimic the artificial bones[7]. The porous structure inside the NiTi SMA allows body tissue to grow inside and the body fluids can be transported through the interconnected pores, which can accelerate the healing process. It can be said that the existence of this porous NiTi SMA gives benefits on growth of new body tissues, making fixation of implant to become more natural and flexible[7]. It is believed that the further development for the porous NiTi SMA will be able to fabricate other artificial organs or tissues that can help more patients which are still waiting for implantation. It gives a hope to the patients or disabilities to have a chance to return back to their normal life. Since it meets the requirement of the biomedical industries, many researches had been carried out on how to fabricate the porous NiTi SMA and also the mechanical properties of the alloy had been conducted and investigated.

1.2 Problem Statement

Porous Material made from biocompatible metals has become the conventional material in the biomedical application like implantation. However, a major problem occurs that the current material may have mismatch of elastic modulus between the bone and metallic materials which then becomes stress shielded eventually leads to bone resorption. Therefore, making porous structure inside the material is important to minimize stress shielding effect and high strength to prevent deformation and fracture. Hence, porous NiTi SMA will be fabricated using powder metallurgy method and the effect of pore forming agent on its mechanical properties will be investigated.

1.3 Objectives

The aim is to investigate the mechanical properties exist in a porous NiTi shape memory alloy within the given time to do this whole project. Thus, the objectives can be achieved by:

1. To fabricate porous NiTi shape memory alloy through powder metallurgy and characterize the porous structure, phase transformation and formation in the alloy.
2. To inspect the effect of pore forming agent towards the compressive behaviour of porous NiTi shape memory alloy.

1.4 Project Scope

In this project, porous NiTi shape memory alloy is fabricated through powder metallurgy method. Nickel (Ni) powder and Titanium Hydride (TiH_2) will be mixed together with various weight percentage of pore forming agent which is Calcium Hydride (CaH_2). The powder mixture was compacted using hydraulic press to produce a cylindrical sample. Next, sintering process will be carried out for the cylindrical

samples in a tube furnace to enhance its strength. Sample characterization will be done after the samples had been fabricated such as X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) to investigate the phase formation while Diffraction Scanning Calorimeter (DSC) was carried out to study the phase transformation of samples. Porosity measurement will be carried out using the porosity equation to calculate the porosity of samples. Mechanical testing such as compression test was carried out to investigate the compressive behaviour of the fabricated samples. The results obtained will be analysed and the mechanical properties of the samples can be determined.

CHAPTER 2

LITERATURE REVEW

2.1 Powder metallurgy Method

Powder metallurgy is a type of metal forming process where includes the metal powders and being pressed and heated under a specific force and temperature. This technique had been existed over 100 years. It is very historical and had been widely used in the industries in that time. The very common powder metallurgy method refers to the pressing and sintering. Initially their focus is on fabrication of metallic compound, but due to its advantages in the aspect of complexity of shape, utilization of material, dimensional control etc, their product more focus on ceramic fibres, intermetallic compounds, metal matrix composites and much more [8].

A. Jabur et al. (2013) [9]study about the characterization of NiTi shape memory alloy with powder metallurgy method. The powder metallurgy method is the same method used in this project as it involves the mixing, compacting and sintering procedures during the fabrication process of samples. The difference is, 21 samples were produced in this study, with different weight percentage of Cr and Al additives. The additives were added into the samples and mixed together before doing compaction. Moreover, the increase in addition of Cr and Al reduce the corrosion rate as well. This literature did not study about the compression behaviour of sample under compressive load where this aspect will be added into this research project later, also the biomedical application of this alloy did not studied in this literature as well. The additives also vary from this literature when compared with the research project later.

A research done by J. Lou, H. He, Y. Li et al (2016) [10]study about the effect of high O contents on the composition of porous NiTi shape memory alloy. The alloy will be aged at different temperatures and holding times and then the microstructure,

phase-transformation behaviour and mechanical properties of the porous NiTi shape memory alloy were investigated. In the process of fabrication, NaCl will be used as pore forming agent, going through mixing, heating, de-salting, vacuum aging and also oxidation aging.

M. Ibrahim (2018) [11] fabricates porous 51(at%) NiTi SMA by using powder metallurgy method to study the effect of time and temperature on the 51(at.%) NiTi SMA. The samples of 51(at.%) NiTi SMA was prepared and then cold pressed. After that, the pressed samples were microwaved sintered at different temperature and different time duration. An electrical discharge machine (EDM) was used to cut the sintered samples for the compression testing and corrosion test.

Another research study written by N. Daawood, A. Abid Ali, A. Atiyah (2019) [12]covers the effect of compact pressure and the copper (Cu) addition to the mechanical properties of porous NiTi shape memory alloy. The porous sample is fabricated by using powder metallurgy method. The method covers the mixing of powders with proper proportion, the compact of the mixture using hydraulic press with various compact pressure and sintering. Microstructure, stress-strain, Young's Modulus were tested on the sample. Transformation temperature and phase identification were tested also using DSC and XRD respectively.

2.2 Self-propagating High-temperature Synthesis (SHS)

Based on a research study by C.L. Chu (2004) [6], they had fabricated the porous NiTi shape memory alloy using combustion synthesis or self-propagating high-temperature synthesis (SHS) for hard tissue implantation. This method involved in lighting up a powder mixture in compressed form either in air or inert atmosphere and a chemical reaction with heat released will be produced. As the result, they had

produced a porous NiTi SMA with porosity about 57.3 vol% and the open porosity is about 86%. The properties of the porous NiTi SMA shown was suitable to be used in the hard tissue implant in future [13]. However, they faced a problem which was undesired compound Ti2Ni precipitate had been formed and they present on or near the grain boundaries of the alloy. It is difficult to be removed and there are still no further studies on how to remove those undesired products.

A research done by M. Kaya, N. Orhan, G. Tosun (2010) [14] had studied about the effect of combustion channel on the compressive strength of porous NiTi shape memory alloy fabricated by using self-propagating high-temperature sysnthesis (SHS). In this study, a different ignition technique called high voltage electric arc was used to ignite the samples during the sintering process. Also the location of ignition was different to obtain different result. It was found that it is achievable that to change the orientation of combustion channel by changing the ignition location but it does not affect much to the porosity of the samples. As a result, the samples has general porosity of 54.2% and an open porosity of 83.4%. The desired product (B2'NiTi and B19'NiTi) formed as well as other compound. The other compound which were undesired can be removed completely by solution treatment under loading. However, they did not give an exact observation about the undesired compound. They use other research studies' opinion to support their view[6][15]. Hence, the elimination of undesired compound need to be investigated further since they knew that the existence may increase the brittleness of the products. Result also shows that Ni content in NiTi matrix strongly affects phase transformation temperatures as phase transformation temperatures decreased with increasing of Ni content of NiTi matrix after aged above 475°C.

2.3 Selective Laser Melting (SLM)

A research study done by M. Taheri Andani, S. Saedi, A. Turabi (2017) [16] is to investigate the mechanical and shape memory properties of NiTi shape memory alloy in dense and designed porous form fabricated by using Selective Laser Melting (SLM) for medical application. The fabrication of porous NiTi samples involves the usage of Phenix-PXM selective laser melting machine where the porous NiTi part was produced through the placement of powder layer by layer in the powder bed through laser radiation. While the dense NiTi samples were produced through the atomization by using Electrode Induction-melting Gas Atomization (EIGA) method. The testing about the stress-strain, shape memory effect and phase transformation for both dense and porous samples were carried out. As the results, five porous samples had characterized two structures with different level of porosity (32% to 69%). The transformation temperature decreased slightly after the SLM method. Both dense and porous samples showed good SME and stability but the porous sample remains 0.5% irrecoverable strain on superelastic behaviour while the dense sample can be entirely recovered.

2.4 Microwave Sintering Method

A study carried out by C.Y. Tang (2011) [17] shows that they had also successfully fabricated the porous NiTi shape memory alloy by using microwave sintering method without using any pore forming agent. the Ni and Ti powders were weighed and blended and then compresses into a green sample inside a rigid die. Then the green sample were put into an adjustable microwave equipment for heating and sintering. The results show that the porous NiTi SMA produced has an increasing porosity ratio (from 27% to 48%) and pore size range also increased when the sintering temperature and holding time is different [18][19]. The results also depict that the

sintering temperature affect the stress-strain behaviour of the porous NiTi SMA significantly but the holding time did not affect much. It can be seen that the fabrication of porous NiTi SMA is very dependent to the temperature and it need to be optimized to obtain a product with its optimum properties. In this literature, the addition of pore forming agent was not studied here but they approach to the process parameter during the sintering process. The sintering process was also different from conventional sintering method as they using microwave to do the sintering. The sintering method can also affect the properties or structure inside the samples and also their uses in biomedical application as supported in the results above [20][21].

2.5 Stress Shielding

It is known that in daily activity when a person moves or doing some action, the muscles and bones inside the person's body will cooperate to complete the moves by transferring the force of expansion or contraction from one to another. Those forces or also known as the compressive stress or strain which enables the person to move freely and hence can do their work smoothly. Some person was suffering in bone fracture or injuries in the bones of some body parts due to accidents, falling object, diseases etc will need bone implantation to help them return to their daily routines. If there is any problem occurs on the bone implants after the surgery, the revision surgery will be carried out to fix the related issues. One of the problem is stress shielding. Stress shielding refers to a reduction of the density of bone as a result of the removal of stress by an implant. Most literature uses hip-joint implantation to discuss the stress shielding of bones [22][23][24][25][26]. Until now, there are no any successful cases shows that the bone implant works perfectly and did not give any side effect for the patients. This is due to the stress transfer between implants and human natural bone is not

homogeneous when the Young's Modulus of bone implants and human bone are not the same [22]. The bone implants usually are stiffer because of higher stress compared to human bone [23]. The implants can carry more load or stress during the stress transfer. Based on Wolff's law, a bone in a healthy person or animal will be remodelled to adopt the load or stress act upon it [23]. The difference in stress carried causing the natural human bone to reduce stress due to less load carry and hence occur stress shielding. This reduction of stress in human bone seems not good because it leads to bone resorption and the bones weakens and have a higher chance to become fracture. The intention of doing hip-joint implantation now causing the serious problems like bone loss and bone deterioration [27]. Bone loss due to stress shielding is the main cause of happen periprosthetic fractures [28]. A lot of studies are needed to make the bone implant to behave more like a real joint.

2.6 Sample Characterization

When a new product is produced by some fabrication technique, it is required to carry out sample characterization to identify the substances produced and its composition. The common sample characterization techniques use here is to identify the microstructure by using Scanning Electron Microscope (SEM), phases formed and its compostion by using X-ray Diffraction (XRD), and the phase transformation during certain heat treatment such as Diffraction Scanning Calorimeter (DSC) on the new product. Based on some literatures from the sample fabrication using powder metallurgy method, A. Jabur et al. (2013) had done sample characterization on the samples fabricated with manipulating the compacting pressure and the chemical additives. Results shows that the compacting pressure and addition of Cr and Al material does not bring effect to the transformation temperature of the NiTi samples.

Besides that, the porosity decreases with the increasing of compacting pressure and high addition of Cr and normal addition of Al, which the Al additives is much more effective than adding Cr. J. Lou, H. He, Y. Li et al (2016) had identified the samples microstructure, phases formed and also phase transformation temperatures on the samples. Adding 50 vol.% of pore forming agent got a sample with porosity approximately 55.2% with open porosity of 95.8%. There is more than 45% of pores had size of greater than 50μm.Results shows that the oxidation will increase the composition of secondary phases instead of the desired phase which is NiTi when the aging temperature increases. Increasing the holding time seems affect the phase transformation as well. Also, the high aging temperature was not recommended here because it will affect the shape memory effect (SME) in samples. M. Ibrahim (2018) characterizes the samples in the three aspects as mentioned in previous literature. As a result, secondary phases was present in the sintered samples, and there were multi-step phase transformation and reverse transformation occurs during the heating process, and the phase transformation temperatures were more than 0℃ during the cooling and heating process based on the DSC curves. N. Daawood, A. Abid Ali, A. Atiyah (2019) characterize the samples from SEM, XRD and DSC, same like previous literature. However, the results of the sample characterization were not mentioned in this study as they focus on its mechanical behaviour.

From the literatures, the sample characterization techniques were very common and did not varies much no matter the how the variables transform. The sample characterization was necessary for the new substance formed.

2.7 Mechanical Testing

There are several method of testing that required on understanding the mechanical behaviour of new substance formed based on different variations and parameters. The testing includes compressive testing, corrosion test, hardness test etc. Compression testing was carried out in a study by J. Lou, H. He, Y. Li et al (2016) and the results obtained shows that the elastic modulus of the samples increases with an increase in aging temperature, but the shape-recovery rate decreases. It was proven that the increasing O content increase the elastic modulus of samples but it decreases the shape-recovery rate. Future studies can be made to improve the problem found and optimize the shape-recovery rate of this kind of alloy. The results obtained from compression testing and corrosion test in a research by M. Ibrahim [11] such that the highest fracture strength and strain as well as the spring back strain and also lowest corrosion rate was found in samples sintered under 700℃. The microwave sintering for the porous NiTi SMA can obtain the samples with low elastic modulus and potentially eliminates the effect of "stress shielding" on the uses in biomedical applications [20][21]. While the corrosion rate obtained in the samples shows that a decrease in sintering temperature will reduce the effect of corrosion of samples. The sample hardness, stress strain, and Young's Modulus had been investigated in a research study by N. Daawood, A. Abid Ali, A. Atiyah (2019). For the result, the hardness for all values increases when the compacting pressure increase, but decreases when the Cu addition increase. The samples also have increasing shape memory effect (SME) properties when the compact pressure and Cu addition increase [29]. Also with the Cu addition, the compressive strength, yield strength and Young's Modulus of elasticity increases. The Young's Modulus obtained was near to the Young's Modulus of the cortical bone. The fabrication of the porous NiTi shape memory alloy in this research has a limitation

on decreasing of hardness when the Cu addition in increasing wt%. Although it has increase SME, lack of strength may cause failure during the functioning in implantation because it may not withstand to work which needs heavy work. Future research can be done on improving the hardness and also optimizing the fabrication method. The result in M. Kaya, N. Orhan, G. Tosun (2010) showed that the compression behavior of a sample is affected with grains orientations [30]. The compressive strength of all the samples produced were higher than the natural human bone and similar Young's Modulus which near to the ideal value of natural bone. So, it is suitable to be used for biomaterials for tissue implants [6]. The test results by M. Taheri Andani, S. Saedi, A. Turabi (2017) also showed that the elastic modulus and ductility for the samples fabricated using SLM method was highly dependent to porosity level and pore structure. It is attainable to reduce the elastic modulus of samples up to 86% by increasing porosity and remain its SME of the samples. The exact way to do so will need the researchers to find out.

The results from literature shows that the mechanical behaviour like hardness, compressive strength, Young's Modulus can be affected by many parameters. The testing needed to be carried out to investigate what is the cause-effect or relationship between the mechanical properties and the variables in samples.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Project Flowchart

The flowcharts below show the process and equipment involved during the whole research project. the project will start with the preparation of samples by fabricating it with several processes and ends with the characterization of sample.

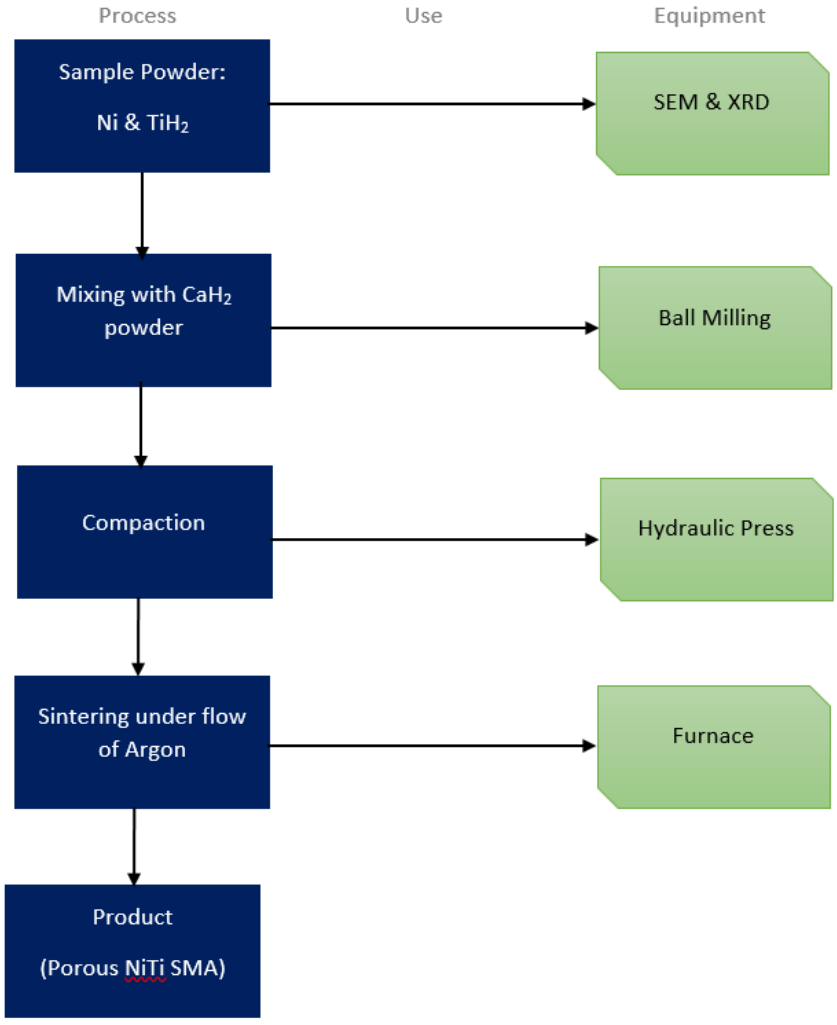

Figure 3.1 The process flowchart of sample preparation with fabrication processes.

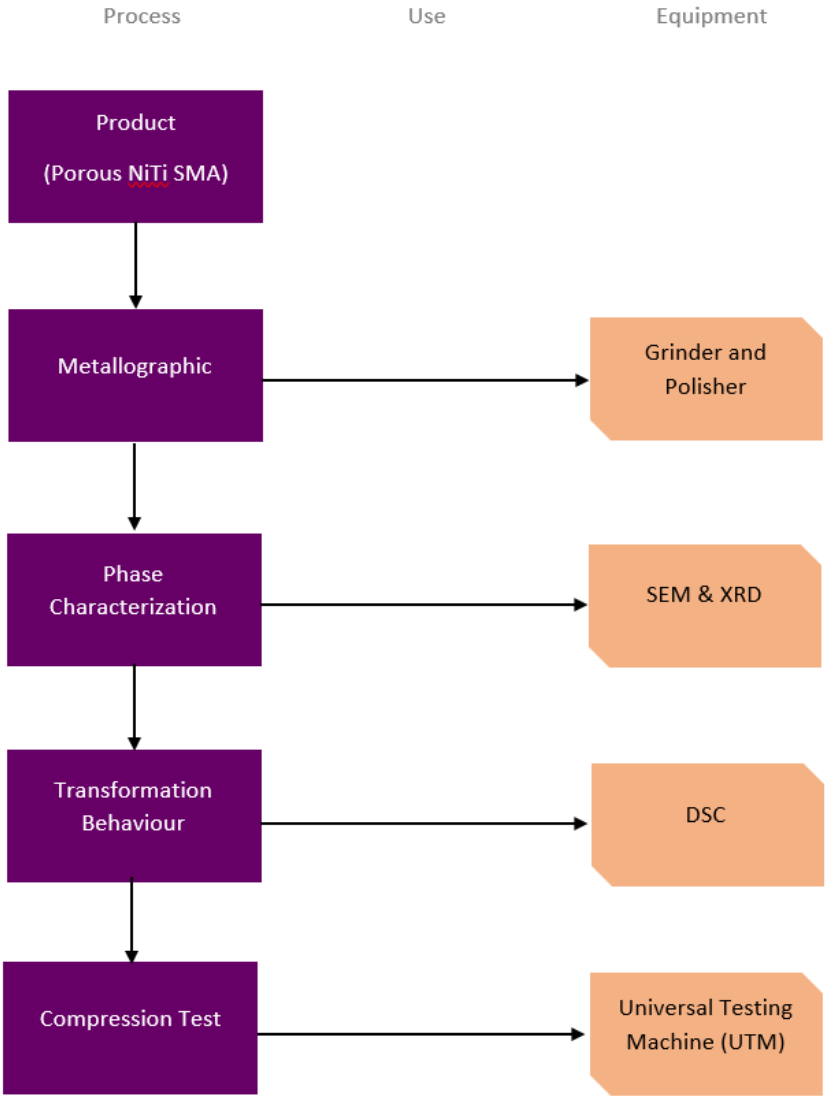

Figure 3.2 The process flowchart of characterization of samples

By referring to the figure 3.1 and 3.2, the overall methodology of this project consist of parts, which are the first part includes the fabrication of samples and the second part where the samples will be characterized. In the sample preparation stage, the powder which are Ni and TiH_2 powder will be prepared. The powders will first undergo SEM and XRD to characterize them individually and to make sure there is no impurities or contamination inside the powder. Then, the powder was mixed together with the addition of pore forming agent, CaH_2 powder using ball milling machine for 24 hours to obtain a homogeneous powder. After that, the compaction and sintering

process will be carried out to enhance the strength of samples. Then, the fabricated samples will be prepared to do characterization. It will first undergo grinding and polishing to observe its microstructure. Porosity measurement was carried out to identify the porosity percentage of the fabricated samples. Next, several testing will be carried out to determine the properties of samples such as SEM for microstructural analysis, XRD for phase identification and DSC for phase transformation. After that, mechanical testing such as compression testing will be carried out using Universal Testing Machine (UTM) to understand the mechanical behaviour of the samples like stress strain behaviour.

3.2 Materials

The powder that will be used in this project are high purity Nickel (Ni) powder and Titanium Hydride (TiH_2) powder. Both powders were obtained from Hwano. The particle sizes of the powders and their chemical purity are shown in the table below. For the pore forming agent, which is Calcium Hydride (CaH_2), was obtained from Sigma Aldrich and the chemical purity also shown in below table.

Table 3.1 Characteristics of Powder

Powder	**Mean Particle Size (μm)**	**Chemical Purity (%)**	**Manufacturer**
Ni	10-30	99.9	Hwano Matr.
TiH_2	1-3	97.5	Hwano Matr.
CaH_2	-	95.0	Merck

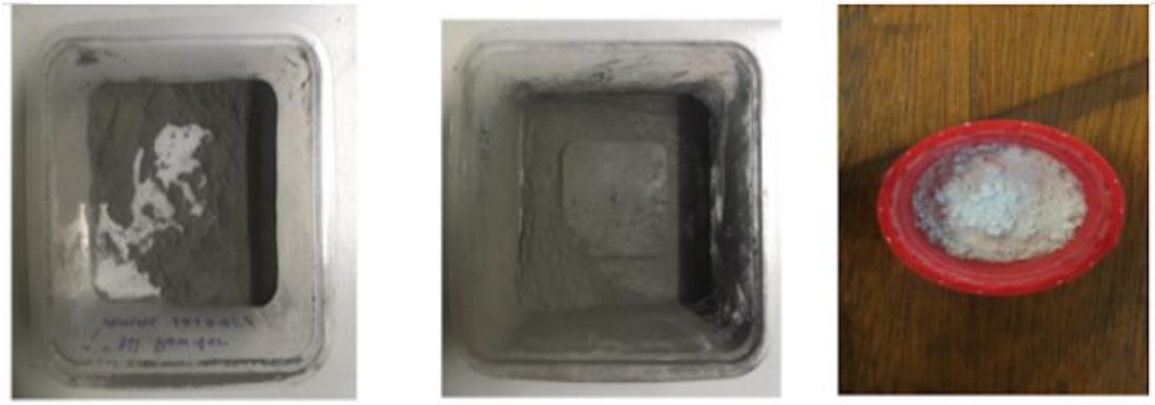

Figure 3.3 From left to right: (a) TiH_2 (b) Ni and (c) CaH_2 powder

3.3 Sample Preparation

3.3.1 Mixing

The Ni and TiH_2 powders will be mixed with addition of pore forming agent, CaH_2 at different weight percentages of 0.25, 0.50, 1.00, 3.00, 6.00, 9.00 and 15.00 wt%. Another sample of NiTi powder with no pore forming agent was also prepared as the reference samples. Then, the powder mixture was mixed in a ball milling machine with a speed of 50rpm to make sure that the powder mixtures were blend homogeneously. The process will be carried out for 24 hours.

3.3.2 Compaction

The NiTi powder was compacted into a 5mm diameter and 12mm height cylinder form. Around 1gram of the NiTi powders are weighted and store it inside a small packet. Each percentage will have 3 specimens that need to do compaction. Then, the weighted powders are poured inside the clean and dry mould and it will be closed. After that, the mould with powder will put inside the PIKE technologies CRUSHIR Digital Hydraulic Press as shown in figure 3.4. The level of the hydraulic press will be pulled to cold-pressed the powder inside at 0.5 tonnes and hold for 3 minutes. Then, the

mould will be taken out from the hydraulic press the compacted specimen will be taken out through the help of tools and a green body of NiTi will be obtained as shown in figure 3.5. The compacted sample is also shown as figure 3.6 as it will looks like a cylindrical solid after the powder undergo compaction.

Figure 3.4 CRUSHIR DIGITAL HYDRAULIC PRESS [31]

Figure 3.5 Green body of NiTi

Figure 3.6 The appearance of compacted sample.

3.3.3 Sintering

The compacted samples with various weight percent of pore forming agent will be put inside the MTI GSL-1100X tube furnace with the flow of Argon gas as shown in figure 3.7. The heating and cooling rate is set to 10 °C/minutes. The schematic diagram is shown below in figure 3.8.

Figure 3.7 MTI GSL-1100X Tube Furnace.

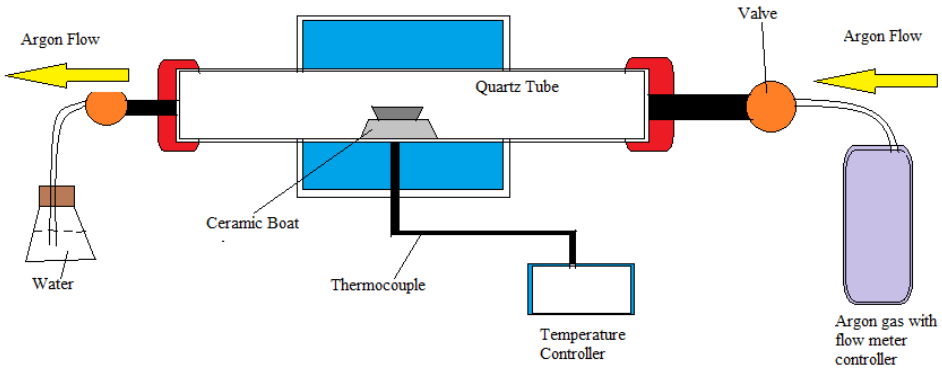

Figure 3.8 Schematic Diagram of the setup for sintering process.

Based on the schematic diagram, one of the flange fitting at the end of quartz tube will be closed and the argon gas will be opened. The flow of argon gas will be controlled in 100cc/ minute. Then, the furnace will be turned on and the program controller was opened to set the parameters. The current temperature, T_1 will be set either room temperature, 40°C, or temperatures that lower than the target temperature,

T_2 by 100℃. The time required to heat the furnace, t_1 was also set by the equation as shown is equation 3.1. A 2 to 3 minutes' time allowance can be set to allow the use to put the samples inside the furnace once it reaches the target temperature. Then, the T_2 is set to 900℃ while the time required, t_2 to sinter the samples in 900℃ is 3 hours, which is 180 minutes. The final temperature, T_3 is as same as T_2 while the t_3 is kept on -121. After all the temperatures and times had been set, the program will run. Once the temperatures in the furnace reaches 900℃, the flange fitting will be opened again and the samples were put inside the furnace. After 3 hours, the tube furnace need to be cooled down first before taking out to prevent scald. After the furnace had been cooled down, the flange fitting will be opened and the sintered samples were taken out.

Equation 1 The equation used for calculating t_1

$$t_1 = \frac{T_2 - T_1}{10}$$

Table 3.2 Temperature and Percentage of Pore Forming Agent used for Sintering

Temperature (˚C)	**Weight Percent of Pore Forming Agent (wt%)**
900	0 (reference sample)
	0.25
	0.50
	1.00
	3.00
	6.00
	9.00
	15.00

3.4 Sample Characterization

3.4.1 Porosity Measurement

The porosity of a sintered sample was determined by weighing the sintered sample's density with a densitometer using Archimedes principle. The equation 2 as shown was used to measure the general porosity of porous NiTi alloy samples, ρ:

Equation 2 Equation used for calculating porosity.

$$p = \left(1 - \frac{\rho}{\rho 0}\right) \times 100\% \quad (1)$$

where ρ is the theoretical density of the respective dense NiTi alloys (6.45 g/cm3) and ρ0 is the apparent density of porous NiTi alloys by dividing the sample's weight by its volume.

3.4.2 X-Ray Diffraction (XRD)

XRD procedures was conducted to identify the phase exist inside the sintered samples. The XRD machines with Cu-kα radiation of 1.54 Å wavelength was used. The samples were ground using different metallographic abrasive paper before the sample analysation was carried out. After that, grinding and polishing process were conducted manually. The samples were then undergoing XRD analysis for phase identification. The results obtained were analysed using High Score Plus software as shown in figure 3.9.

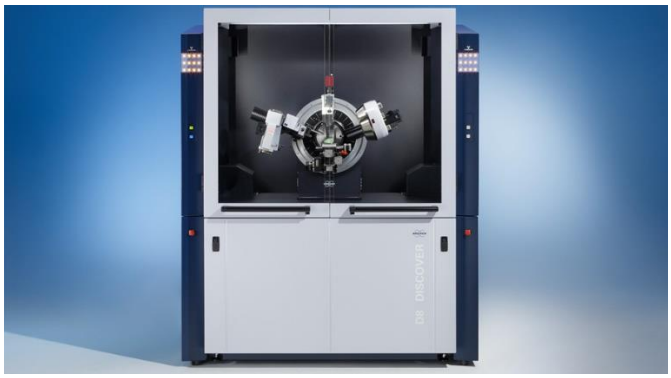

Figure 3.9 The XRD machine.

3.4.3 Scanning Electron Microscope (SEM)

SEM were used to characterize the microstructure exist inside the samples. The sintered samples will be cut in a smaller size and mounted using epoxies. Then, the

samples mounted with epoxies was grounded with abrasive paper. After that, the samples were polished to 1 µm using diamond suspension finish. In this project, a SEM EDAX machine as shown in figure 3.10 will be used to do the sample characterization.

Figure 3.10 SEM EDAX Machine.

3.4.4 Differential Scanning Calorimeter (DSC)

The reference sample and the NiTi samples with different weight percentage of pore forming agent were cut into a small segment. Each of the segmented sample was put into the DSC Machine Q20 to be initially cooled from room temperature to -30℃ at a scanning rate of 10℃/min and then heated up until 80℃ in the same scanning rate. Subsequently, the sample was cooled again to -30℃ at the same scanning rate. Nitrogen gas was used for this experiment to flush the chamber and boost the cooling process so that it can reach to the target temperature. The nitrogen gas can also help to prevent the condensation of water vapour and the sample to be oxidized. The result about the heat flow of sample against the temperature will be obtained.

Figure 3.11 The DSC Machine Q20

3.4.5 Compression Testing

The compression testing had been carried out to investigate the mechanical behaviour of samples produced. The testing was carried out using the Instron 3367 Universal Testing Machine (UTM) with Instron Bluehill. The UTM machine is used to carry out the practical compression test while the Instron Bluehill is a software which connects to UTM machine to collect the experimental data. During the preparation of experiment, compression load cell will be installed at both end of the UTM machine. The maximum force for load cell can reach 40kN. After that, the upper load cell will be lifted up by pressing the level up button and the specimen is put into the center of load cell using a tweezer since the specimen is small. Next, the upper load cell moved down until the surface of load cell touches the surface of specimen. The setting was done in the Instron Bluehill software. The strain rate of this experiment is fixed into 0.01mm/min. The diameter and the length of every specimen will also be measured and input into software such that the diameter is 5mm for all specimens while the length of specimens varies in between 6 to 7mm. Then, the raw data will be saved and the data that need to be displayed also will be set by using the software. After all things were