Manufacture of titanium alloys by powder metallurgy for biomedical implants

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The Manufacture of Titanium Alloys by Powder Metallurgy for Biomedical Implants

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School of Mechanical & Aerospace Engineering

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in fulfilment of the requirement for the degree of
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The Manufacture of Titanium Alloys by Powder Metallurgy for Biomedical Implants

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Abstract

With the increasing use of biocompatible material in modern surgery as an implant, there has been greater interest and emphasis placed on the mechanical performance of the material. Replacement of bone and joints (e.g. hips, knees, intervertebral spinal fixators) are the most subjected to extreme mechanical loading and wear in a corrosive environment.

This project aims in the study of the application of powder metallurgy for the production of biomaterial implants (e.g. Ti6Al4V and Ti-Si-Zr) with engineered porosity and mechanical properties (i.e. lower yield strength).

While Ti6Al4V has been used for biomaterial applications for many years, the use of Ti-Si-Zr is relatively new. The unique choice of this composition was due to Titanium(Ti) had a long history as a biomaterial. The inclusion of silicon (Si) is due to recent research that found it was present in rich concentration at the end of growing bone and therefore could be considered a promoter of osseointegration. Zirconium was chosen because it lowers the Young's modulus of the implant.

Up to now, not much work has been reported on the manufacture of Ti6Al4V and Ti-Si-Zr using mechanical alloying. Therefore the focus of this projects will be shaping and forming of Ti6Al4V and Ti-Si-Zr material along with microstructure composition and porosity.

About the Author

“Mr. Goi Lim Sheng Kip graduated with Bachelor of Engineering (Honours) in Manufacturing Engineering from University of Birmingham, UK in 2000. He joined NTU in October 2002 as student under the supervision of Dr Anders E. W. Jarfors of SIMTech and Assistant Professor David Lee Butler.”

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Acknowledgement

I would like to thank several people for their kindness and support given in the making of this research work a meaning and fruitful one. This work could not have been completed without the help and motivation given by Dr. Yong Ming Shyan John, Dr. Anders E. Jarfors and Assistant Professor David Lee Butler. These people had put in countless effort and guidance into me. Their knowledge in each of their individual field was most rewarding as each of them had given me a clear direction of this project and their advise on organizing and writing of this thesis. I am grateful to Dr. Gu Yan Wei for her assistance on characterisation the samples and her undying spirit of imparting her knowledge to me. Also thanks to the friends around me, for their encouragement, morale support and help in the experiment to be carried out.

Special thanks to Ho Ming Kuang, who has given his precious time in assisting me in the machine operation and technical problems of the furnaces in the sintering laboratory.

I would not be what I am now if not for my family. To my parents, I own most of everything too. Words cannot tell the much thanks and gratitude I had for them, in getting through the tough time and made me stay focused to do what I am doing now. To my brother Lim Ping in supporting my decision of continuing my further studies. I would like to dedicate this work to everyone in my family and friends at my heart.

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1 Introduction

The principal requirements for an implant, in contact with blood and other tissues in the human body, are that it must be biocompatible, nontoxic and durable. Furthermore, the material ought to be nonirritating to tissue, resistant to platelet and thrombus deposition, non-degradable in the physiological environment, and neither absorb blood constituents, nor release foreign substances into the blood stream[1].

Design consideration is another factor, which needs to be addressed. Implants should mimic the characteristics of the tissue they replace without hampering the surrounding anatomical structure. The biomaterial chosen must be easily available, inexpensive, easily machinable, sterilizable, and have a long storage life. Material selection will also be dictated by the strength requirement, thermal conductivity and mechanical properties for the implant being made. Biomaterials include a wider range of types including ceramic, polymer, composites and metals. Metals are commonly utilized as biomaterials due to their formability and unbioreactivity.

Several metals have been used as passive substitutes for hard tissue substitution such as hip or knee joints, for fracture healing assistance, as plates and screws, spinal fixation devices and dental implants because of their superb mechanical properties and corrosion resistance. Other metallic alloys are employed for roles that are more active in devices such as vascular stents, catheters guide wires, orthodontic archwires and cochlea implants.

1.1 Objective of this project

The objective of this project is to develop an implant, which can satisfy the biocompatibility requirements stated above. In addition, the mechanical properties should be similar to those of bone (in particular Young's Modulus) which can be achieved by engineered porosity.

More specifically, the objective is to develop a suitable manufacturing method to engineer porosity with respect to a pore size of between 100-500 μ m, which will allow

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human tissue ingrowths and body fluid transmission[2]. The controlled distribution and a suitable level of interconnectivity within the implant will encourage cell ingrowth as was an appropriate degree of vascularity..

1.2 Scope

The use of powder metallurgy in manufacturing has been rather limited due to the inability to achieve full densification a requirement for many engineering applications. However, biomaterial implants generally require a relatively low Young's modulus and good distribution of porosity. Utilizing this perceived disadvantage in powder metallurgy and applying it in the manufacturing of biomaterials should be beneficial for Young's modulus (relative to the bone) and for a good distribution of pores. By employing powder metallurgical techniques, it is hoped to achieve the above desired material and mechanical properties.

There are several aspects, which will be addressed in this project and they are as follows:

- Mechanically alloying of the powder,
- Sintering of the alloyed powder, and
- Characterization of the sintered parts (e.g. elements, phase formation pore distribution and average pore sizes)

1.3 Report Outline

Chapter 2 will provide a review of the biomaterials covering the various types of implant materials as well as the requirements.

Powder manufacturing methods will be introduced in chapter 3 and in particular mechanical alloying.

Chapter 4 will provide a review of manufacturing methods, which can produce porous metals. Specifically, sintering is covered in details with both solid and liquid phase sintering being reviewed.

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The experimental plan is described in Chapter 5 with mechanical alloying, sintering parameters and characterization of the sintered samples.

The results and discussion of mechanical alloying of both Ti6Al4V and Ti-Si-Zr are described in Chapter 6. Grain distribution and contamination issues are presented and analysed.

Finally some conclusion will be drawn from the results presented in Chapter 6 and suggestions for future works will be proposed in Chapter 7.

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2 Biomaterial Requirements

This chapter gives a brief review of how biomaterials have developed over the years and the various types of biomaterials and their applications.

2.1 What are biomaterials?

There are many ways to define a biomaterial, but one widely accepted definition is “any substance synthetic or natural in origin which treats, augments, or replaces any tissue, organ or function of the body”[3].

Biomaterials enhance the quality of life for an ever-increasing number of people each year. The range of application of biomaterials is vast and includes joint and limb replacements, artificial arteries and skin, contact lenses, and dentures. While the implementation of some of these materials may be for medical reasons such as the replacement of diseased tissues required to extend life expectancies, other reasons may include purely aesthetic ones including breast implants. The biomaterials community is creating new and more advanced implant materials and techniques to meet this demand, but also to aid the treatment of younger patients where the necessary properties are even more demanding. A counter force to this technological push is the increasing level of regulation and the threat of litigation. To meet these conflicting needs it is necessary to have reliable methods of characterisation of the material and material/host tissue interactions.

2.2 Bone

Material constituents and structural organization of bone influence the ways in which bone responds to mechanical loading. The composition and the structure of bone yield a material that is strong for its relative lightweight (due to the bone properties)[4].

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2.2.1 Bone Materials

The major building blocks of bone are calcium carbonate, calcium phosphate, collagen and water. Relative percentages of these materials vary with the age and health of the bone. Calcium carbonate and calcium phosphate generally constitute approximately 60% to 70% of dry bone weight. These minerals give its stiffness and are the primary determiners of its compressive strength. Minerals like magnesium, sodium and fluoride are vital for the bone’s structural and metabolic roles in the bone growth and development. Collagen is a protein that provides bone with flexibility and contributes to its tensile strength.

Water content within the bone makes up 25% to 30% of the total bone weight. The presence of water within the bone is an important contributor to its strength[4].

2.2.2 Bone Properties

Hard tissues such as bone are porous materials, which favour firm fixation and body fluid transmission. Implant materials with porosity in the range of 30–90% or 20-50 volume percent[5] and open pores in diameter range 100–500µm[6, 7] are required to enhance tissue ingrowth and prosthesis fixation. Bone tissues grow into the open pores of skeletal prostheses, creating a highly convoluted interface[8]. For the design of prosthesis, bone mechanical properties are of first attention. Possessing these critical values of strength and modulus, this can be exploited as in fabrication of artificial bone models or finite element analyses to evaluate alternative designs. The below Table 1 shows some of the mechanical properties of the male human femoral bone aged between 35 and 45 years.

Table 1 The mechanical properties of a male bone[9]

Mechanical properties of bone	
Elastic modulus (E)	15.2 GPa
strength (σ_f)	170 MPa
Fracture toughness (K_{IC})	6.4 MPa m ^{1/2}
Work of fracture (W_f)	3.4 kJ m ⁻²

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2.3 Types of Bio-implants

Biomaterial encompasses a wide range of material which are generally classified under two headings of bio-implants:

- Non-metallic (e.g. Ceramics, Polymers and Composites)
- Metallic

Bio-implants can be roughly divided into three main types governed by how would the human body-tissue would respond. In broad terms, inert (more strictly, nearly inert) materials illicit no or minimal tissue response. Active materials promote bonding to surrounding tissue with, for example, new bone growth being motivated. Degradable, or resorbable materials are integrated into the surrounding tissue, or may even dissolve completely over a period of time. Metals are typically inert, ceramics may be inert, active or resorbable and polymers may be inert or resorbable.

2.3.1 Ceramics

Ceramic are refractory, polycrystalline compounds, usually inorganic, they include silicates, metallic oxides, carbides and various refractory hydrides, sulfides and selenides. Exception to this are the covalently bonded ceramics such as diamond and carbonaceous structures like graphite and pyrolyzed carbons.

In recent years, researchers have realised that ceramics and their composites can be used to augment or replace various parts of the body, particularly the bone and lately ceramics have been used for this purpose. Ceramic's inertness to body fluids, high compressive strength and aesthetically pleasing appearance have led to the use of ceramics in dentistry as dental crowns. Some carbons have found use as implants especially for blood interfacing applications such as heart valves. Due to their high specific strength in fibres and their biocompatibility, ceramics are also utilized as a reinforcing component of composite implant materials. Examples are tensile loading such as artificial tendon and ligaments.

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The only major shortcoming of ceramics is the difficulty to shear plastically due to the (ionic) nature of the bonding and minimum number of slip systems. This characteristic make ceramics non-ductile and are responsible for almost zero creep at room temperature. Ceramics do not go through plastic deformation so are they susceptible to notches and microcracks. They will fracture elastically with initiation of cracks. Stress at the crack tips could be many times higher than the stress in the material away from the tip, resulting in a stress concentration that weakens the material considerably. Ceramics have low tensile strength compared to compressive strength.

Advantages of ceramics are their high melting temperature and low conductivity of electricity and heat. These characteristics are due to the bonds within the ceramics.

Ceramics employed for implant fabrication can be classified as nonabsorbable (relatively), bioactive or surface reactive (semi) and biodegradable or resorbable (non-inert). Alumina, zirconia, silicon nitride and carbons are inert bioceramics. Certain glass ceramics and dense hydroxyapatites are semi-inert (bioreactive) and calcium phosphates and calcium aluminates are resorbable ceramics[1].

2.3.2 Polymers

Synthetic polymeric material have been widely used in disposable medical supplies, prosthetic materials, dental materials, implants, dressing, extracorporeal device, encapsulants, polymeric drug delivery systems, tissue engineered products and orthodoses.

Advantages of polymeric biomaterials are as follows:

1. Compared to metal or ceramics, polymers are easy to manufacture and shape into:
  - Film
  - Sheet
  - Fibres and other
2. Ease of secondary processability
3. Reasonable cost (as in a small amount (few grams) of raw material can produce a large quantity of product)
4. Available in desired mechanical and physical properties

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Requirements of polymeric biomaterials are similar to other biomaterials, manufacturability is given in Table 2

Table 2 Requirements of Biomedical Polymers[1]

Properties	Description
Biocompatibility	Noncarcinogenesis, nonpyrogenicity, nontoxicity and nonallergic response
Sterilizability	Autoclave, dry heating, ethylenoxide gas and radiation
Physical property	Strength, elasticity and durability
Manufacturability	Machining, molding extruding and fibre forming

2.3.3 Composite

Composite materials are solids that contain two or more distinct constituent materials or phases on a scale larger than the atomic. Their properties are such that the elastic modulus are significantly altered in comparison with those of homogeneous materials. Reinforced plastic such as fibreglass and natural bone are viewed as composite, but alloys such as brass are not.

A composite material offers a variety of advantages in comparison with homogeneous materials. Scientists or engineers can exercise considerable control over the material properties. There is the potential for stiff, strong, lightweight materials as well as for highly resilient and compliant materials. In biomaterials, it is important that each constituent of the composite be biocompatible. Moreover, interface between constituents should not be degraded by the body environment. Some applications of composite biomaterials are:

- Dental filling composite
- Added in-between the surface of the bone and implant (e.g. in Total Hip Replacement)
- Made as Cup for fitting in the Ball in Total Hip Replacement
- Orthopedic implants with porous surface

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2.3.4 Metals

Metals are used as biomaterials due to bio inertness and mechanical properties. As electrons are independent in metals, they are quick in transferring electric charges and thermal energy. Electrons are also mobile which acts as the binding forces to hold the positive metal ions together. When attraction is strong, the closely packed atomic arrangement results in high specific gravity and high melting points for most metals. Since metallic bonds are essentially non-directional, the position of the metal can be altered without destroying the crystal structure resulting in plastic deformation of the solid[10].

2.3.4.1 Vanadium Steel

The first metal alloy developed specifically for human use was "vanadium steel" in the early 1900's. As early as the first bone plate implants, surgeons acknowledged material and design problems that consequently resulted in early loss of implant function, as supported by mechanical failure, corrosion, and poor biocompatibility. Vanadium steel is no longer employed in implants since its *in vivo* corrosion resistance is inadequate[10].

2.3.4.2 Stainless Steel

Stainless steels, especially Types 316 and 316L, are most widely used for implant fabrication. Stainless steel is suitable for implantation into human body as it has a low content of impurities and a passivated surface. Forged stainless steel have greater yield strength than cast stainless steel, but a lower fatigue strength than other implant alloys. Nevertheless, stainless steel is more ductile and more easily machined and recent advancements have significantly improved its properties. Stainless steel is no longer used routinely, in femoral components from the standpoint of erosion, biocompatibility, and fatigue life, stainless steel is inferior to other super alloys[10].

The only difference in composition between 316L and 316 stainless steel is the content of carbon (0.08% to 0.03%) see Table 3. A wide range of properties exists depending on the heat treatment (annealing to obtain softer materials) or cold working (for greater strength and hardness). 316L stainless steels will inevitably corrode within the body in an

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extremely stressed and oxygen depleted region, such as contact under screws or fracture plates. Thus, stainless steels are suitable to use only as temporary implant devices, such as fracture plates, screws and hip nails[10].

Table 3 Typical Composition of 316L[1]

Elements	Composition(%)
Carbon	0.03 max
Manganese	2.00 max
Phosphorus	0.03 max
Sulphur	0.03 max
Silicon	0.75 max
Chromium	17.00-20.00
Nickel	12.00-14.00
Molybdenum	2.00-4.00

2.3.4.3 CoCr Alloy

Two basic types of cobalt chromium alloys exist. One is the CoCrMo alloy, which is typically used to cast a product and the other is the CoNiCrMo alloy, which is usually wrought by (hot) forging (Table 4). Castable CoCrMo alloy has been utilized for many decades in dentistry and recently, in making synthetic joints. The wrought CoNiCrMo alloy is used in the stems of prosthesis for intensively loaded joints such as for the knee and hip. Cobalt-based alloys are highly resistant to corrosion and especially to attack by chloride ions when exposed to it for example the crevice or gap corrosion. As in all highly alloyed metals in the body environment, galvanic corrosion occurs, but to a lesser extent than in the iron-based alloys.

Cobalt-based alloys are quite resistant to fatigue and to cracking caused by corrosion. However, as is true of other alloys, cobalt based alloys may degrade because of fatigue fracture (but less often than stainless steel stems). The abrasive wear properties of the wrought CoNiCrMo alloy are alike to the cast CoCrMo alloy.

Wrought CoNiCrMo alloy possessing superior fatigue and ultimate tensile strength make it suitable for the applications, which require long service without fracture or stress fatigue. Such is the case for the stems of the hip joint prosthesis. Both the cast and

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wrought alloys have excellent corrosion resistance. The modulus of elasticity for the CrCo alloys does not change with the changes in their ultimate tensile strength. The numbers are higher than for other materials such as stainless steels[10].

Table 4 Typical composition of cobalt-chromium implants material [1].

Elements	CoCrMo		CoNiCrMo	
	Min	Max	Min	Max
Chromium	27.0	30.0	19.0	21.0
Molybdenum	5.0	7.0	9.0	10.5
Nickel	-	2.5	33.0	37.0
Iron	-	0.75	-	1.00
Carbon	-	0.35	-	0.025
Silicon	-	1.00	-	0.15
Manganese	-	1.00	-	0.15
Tungsten	-	-	-	-
Phosphorus	-	-	-	0.015
Sulphur	-	-	-	0.010
Titanium	-	-	-	1.0
Cobalt	Balance	Balance	Balance	Balance

2.3.4.4 Titanium based alloys

Use of titanium as an implant dates back to late 1930's. Titanium was found to be tolerated in cat femurs, as was stainless steel and vitalium (a CoCrMo alloy). Titanium exhibits good properties like low weight and good mechanical and chemical properties which are salient features for implanting applications. One titanium alloy; Ti6Al4V, is extensively used to manufacture implants. The main alloying elements of the alloy are aluminium (5.5 - 6.5%) and vanadium (3.5 - 4.5%) (Table 5). Whilst the strength of the titanium alloys varies from lower than to equal to that of 316 stainless steel, when comparison is made to the specific strength (strength divided with density), titanium alloys surpass any other implant material. With poor shear strength, titanium it is less likely to be made into bone screws, plates and similar applications.

Titanium also tends to seize when in sliding contact with itself or other metal. Titanium-based alloys have a high co-efficient of friction that can cause problems. Wear particles

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are formed in bone if a piece of bone rubs against the implant, or if two parts of an implant rub against one another. Therefore, implants of titanium upon titanium generally are not used as joint surfaces. Titanium derives its corrosion resistance from the formation of a surface oxide film. Under 'in vivo' conditions, the oxide is the only stable reaction product[10].

Table 5 Typical composition of Ti6Al4V[10]

Elements	Composition(%)
Aluminium	6.00
Vanadium	4.00
Nitrogen	0.05
Carbon	0.08
Hydrogen	0.0125
Iron	0.25
Oxygen	0.13
Titanium	Balance

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2.4 Requirements of Implants

The requirements of a biomaterial implant for an orthopaedic application are summarised in Table 6[11, 12]:

Table 6 The requirements of an orthopaedic application for Implants

Biocompatibility	Biofunctionality	Manufacturing
Tissue reaction	Mechanical Properties	Fabrication methods
Change in properties	Elasticity	Consistency and conformity to all requirements
Mechanical	Yield Stress	Quality of raw materials
Physical	Ductility	Superior techniques to obtain excellent surface finish or texture
Chemical	Toughness	Capability of material to get safe and efficient sterilization
Degradation leads to	Time Dependent deformation	Cost of product
Local deleterious changes	Creep	
Harmful systemic effects	Ultimate strength	
	Fatigue strength	
	Hardness	
	Wear	

After deciding on the requirement of an implant for an orthopaedic application, a suitable manufacturing process needs to be chosen. There are many processes for manufacturing of an implant, for example, casting, hot or cold forging, drawing and others. These methods involve the application of a large amount of heat and energy, which are relatively expensive.

Powder metallurgy and pressure working of metals are most often used to fabricate implants. Such implants have a number of features, for example porosity which reduces

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the article weight and furthermore, promotes joining of the implant and the bone tissue. The mechanical properties of a porous article are different from the properties of compact material. The operating characteristics of the articles depend on their fabrication technology, therefore powder metallurgy was chosen in the present study.

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3 Powder Manufacturing Methods

There are five basic techniques of producing powders. These are:

- crushing
- agglomeration
- chemical processing
- atomization of melts
- mechanical alloying

Each method can be further sub-divided and a range of combinations can also produce powders from each group. As a result there is a wide range of manufacturing routes available for powders with their own particular characteristics. Each of the production methods are discussed in detail below.

3.1 Crushing

Crushing, along with milling and grinding are, in general, employed in the production of ceramic powders. However, it is also commonly used to manufacture some metal and metal alloy powders.

The most widespread use is in the manufacture of alumina and zirconia powders. The feed oxide is melted using graphite electrodes, which are then allowed to solidify into a huge block. The block is then broken down and sized. This route is also known as the "Bake and Bash" method! The powders produced are compact but they also have a coarse, irregular, and blocky morphology.

For metal alloys such as CuNiIn, rolling is sometimes used to produce a flake-shaped product. This is then broken up to produce a powder.

Cryogenic milling is used to break down some metals, which become brittle at low temperatures. When used in the manufacture of molybdenum powder this method is known as the *Coldstream* process. Liquid nitrogen is used to cool the bulk material and projected in two opposing gas streams. At the crossover point of the two streams the

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material is broken down and the process is repeated until a desired size distribution is obtained.

Metal alloy powders can also be made by the hydride-dehydride method. In this method, metal alloys (usually in ingot form) are hydrided to create brittle phases and disintegrated into powder, for example, with a ball mill. When the material reaches a suitable size range it is then de-hydrided in a vacuum furnace to leave a metal or metal alloy powder. This routine is applied in the manufacture of titanium and titanium alloy powders. The powder is generally blocky in form and can contain high levels of hydrogen and oxygen[13].

3.2 Agglomeration

The most frequent method of agglomeration is where constituents are physically mixed jointly with an organic binder. The solvent is then removed and the resultant material sized. The binder should be burnt off during spraying. This procedure is used in the making of NiAl, AlSi-polyester powders.

The exercise of spray drying has become another common practice for the agglomeration of powders. A slurry is created with the constituents and this is then supplied into a rotary spray head. Here, the slurry is turned into an atomised cloud, which will solidify with the assistance of an opposing warm airflow to generate a powder. This method is used for ceramics such as zirconia and cermets such as WC-cobalt. The powder is largely spherical but in the as-spray dried state can be porous and reduced to powder. The material is commonly densified and stabilised by sintering and/or spray densification.

Mechanical agglomeration is an additional method (e.g. the Hosakawa method) where, for instance, a hard constituent is mechanically forced into a softer matrix particle to form a composite powder. Certainly, simple ball grinding can also be exploited to mechanically alloy two or more constituents together.

Sintering and spray dry process can be used as two different processes for powders processing. The constituents are mixed together and heated to get some solid-state

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diffusion going and then the resultant product is crushed. A number of repeated cycles can be used to promote further alloying in which case the powder is called a "reacted" powder[13].

3.3 Chemical Processing

There are numerous chemical methods for producing powders. Generally, chemical methods produce very fine powder particle sizes. Such techniques include:

- Sol Gel-Techniques
- Chemical Precipitation
- Reduction Process
- RF-plasma reaction Synthesis
- Reduction (hydrogen in an autoclave to reduce metal salts to the metal)
- Decomposition (eg metal carbonyls)
- Electrolytic

In Chemical Vapour Deposition (CVD), heating in a hydrogen atmosphere enables the following reaction to take place to make TiC powder

Sol Gel was originally developed to make ceramic materials for the nuclear industry in order to avoid the dust generated in grinding and sieving processes. While generally fine (generally less than 20mm) such powders have excellent flow characteristics.

Another interesting chemical method is INCO's unique carbonyl process which is used to produce clad powders such as nickel - graphite[13].

3.4 Atomisation of Melts

There are a number of atomisation techniques which all rely on the production of a molten pool as the source. Atomisation methods include Rotating Electrode, Vibrating

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Electrode (arc), Centrifugal atomisation (from a melt), water atomisation and gas atomisation. However, by far the most commonly used methods are either water or gas atomisation[13]. Here, molten metals are poured from a melt through an atomising gas or water nozzle to produce a finely atomised stream. This stream is then allowed to fall down a tower where it solidifies and is collected. In this process, the cheapest method is that of water atomisation whereas the most expensive is argon atomisation. The advantage of the latter process is the better control of oxygen levels in oxygen sensitive materials such as MCrAlY's[13].

3.5 Mechanical Alloying

Mechanical alloying (MA) is a solid-state powder processing technique, which involves repeated welding, fracturing and rewelding of powder particles in a high-energy ball mill. It was originally developed for oxide-dispersion strengthened (ODS) materials like nickel- and iron-base superalloys for applications in the aerospace industry, corrosion-resistant alloys and alloys of otherwise immiscible components. MA is capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or prealloyed powders. Phases of non-equilibrium alloy that are synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures and amorphous alloys. Recent progress in these areas and also on disordering of ordered intermetallics and mechanochemical synthesis of materials have been significantly re-examined after considering the process and process variables involved in MA. Wherever potential comparisons have been prepared on the product phases attained by MA with those of rapid solidification processing, another non-equilibrium processing technique.

When mechanically alloying blended elemental powder mixtures, interdiffusion between the components occurs and, when conditions permit, solid solutions form. This solid solubility limit is expected to increase with milling time as diffusion progresses and reach a super-saturation level; beyond which no further extension of solid solubility occurs (Figure 1). This saturation value has been listed as the solid solubility level achieved by MA. On the other hand, when the two component metals form an isomorphous system, the lattice parameter of one of the metals decreases and that of the other increases with

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milling time. Once steady-state conditions are established, the two lattice parameters merge and a homogeneous solid solution with the expected lattice parameter is formed (Figure 2).

Figure 1 Schematic diagram showing the variation of solid solubility with time during mechanical alloying of metal powder mixtures

Figure 2 Schematic variation of the lattice parameter (solid solubility) of the individual component phases with milling time in a binary alloy system

Amorphization was explained as a diffusion-controlled solid-state chemical reaction initiated by the interface of these elemental layers. Two prerequisites should be fulfilled for that purpose:

- large negative enthalpy of mixing of the alloying elements, and
- one of the alloying elements should be a fast diffuser in the other

Another kind of amorphization by MA is the initial formation of crystalline intermetallic compound, which in turn transform to amorphous state on continued milling. This transformation can be attributed to the accumulation of point defects which raise the free energy of crystalline phase above that of their amorphous counterpart[14].

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In order to achieve the required product phase and/or microstructure, mechanical alloying involves the optimization of a number of variables. These variables are important parameters that have an effect on the final constitution of the powder: type of mill, milling container, milling speed, milling time, type, size and size distribution of the grinding medium, ball-to-powder weight ratio, extent of filling the vial, milling atmosphere, process control agent and temperature of milling.

All these process variables are not completely independent. For example, the optimum milling time depends on the type of mill, size of the grinding medium, temperature of milling, ball-to-powder ratio, etc. Even then, we will discuss, in the following paragraphs, the effect of these variables (Assuming mostly that other variables have no significant effect on the specific variable being discussed) on the final product obtained after MA.

3.5.1 Type of mill

There are several different types of mills for accomplishing MA. These mills differ in their capacity, speed of operation, and their ability to control the operation by varying the temperature of milling and the extent of minimizing the contamination of the powders. Depending on the type of powder, the quantity of the powder, and the final constitution, a suitable mill can be chosen. Most commonly, however, the SPEX shaker mills are used for alloy screening purposes. The Fritsch Pulverisette planetary ball mills or the attritors are used to manufacture large quantities of milled powder. Specially designed mills are used for specific applications[15, 16].

3.5.2 Milling container

The material employed for the milling container (grinding vessel, vial, jar, or bowl are some of the other terms used) is important because due to impact of the grinding medium on the inner walls of the container, some material will be dislodged and be incorporated into the powder.

If the material of the grinding vessel is dissimilar from that of the powder, then the powder may be contaminated with the grinding vessel material. On the other hand, if the

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two materials are the same, then the chemistry may be altered unless proper precautions are taken to compensate for the additional amount of the element incorporated into the powder. Typical materials used for making grinding vessels are Hardened steel, tool steel, hardened chromium steel, tempered steel, stainless steel, WC-Co, WC-lined steel and bearing steel. The shape of the container also seems to be important, especially the internal design of the container. Both flat-ended and round-ended SPEX mill containers have been used. Alloying was found to occur at significantly higher rates in the flat-ended vial than in the round-ended container[17].

3.5.3 Milling speed

It is easy to realize that the faster the mill rotates the higher would be the energy input into the powder. Depending on the design of the mill there are certain limitations to the maximum speed that could be employed, for example, in a conventional ball mill increasing the speed of rotation will increase the speed with which the balls move. Above a critical speed, the balls will be pinned to the inner walls of the vial and do not fall down to exert any impact force. Therefore, the maximum speed should be just below this critical value so that the balls fall down from the maximum height to produce the maximum collision energy.

Another limitation with maximum speed is when at high speeds (or intensity of milling), the temperature of the vial may achieve a high value. Advantageous in some cases where diffusion is required to promote homogenization and/or alloying in the powders. In other cases it is a disadvantage as it accelerates the transformation process and results in decomposition of supersaturated solid solution or other metastable phase formed during milling. Another shortcoming of the high temperature is that it will contaminate the powder[18]. As when nanocrystal were fashioned during the milling, the crystal's average sizes increases and internal strain decrease at higher milling intensities due to the enhanced dynamical recrystallisation[19]. The maximum temperature attained varies for different types of mills and the values fluctuate widely.

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3.5.4 Milling time

The most important parameter is the milling time. The time was chosen in order to accomplish a steady state between the fracturing and welding of the powder particles. Times will vary due to the type of mill employed, intensity of milling, ball-to-powder ratio, and temperature of milling. The appropriate times are determined for each combination of the parameters and for the particular powder system under consideration. However, contamination level and undesirable phases will arise if the milling time of the powder is longer than required. Therefore milling time is optimised to attain the desired powder.

3.5.5 Milling Media

Hardened steel, tool steel, hardened chromium steel, tempered steel, stainless steel, WC-Co, and bearing steel are the most frequent types of materials utilized for the grinding medium. The density of the grinding medium ought to be high enough so that the balls generate sufficient impact force on the powder.

However, as for the grinding vessel, some special materials are made use of for the grinding medium and these comprise of copper[20], titanium[21], niobium[22], zirconia (ZrO_2)[23, 24], agate[25], yttria stabilized zirconia (YSZ)[26], partially stabilized zirconia + yttria[27, 28], sapphire[29], silicon nitride (Si_3N_4)[30], and Cu-Be[31]. It is always desirable, whenever possible, to have the grinding vessel and the grinding medium made of the same material as the powder being milled to stay clear of cross contamination.

The volume of the grinding medium also has implication for the milling efficiency. Generally speaking, a large size (and high density) of the grinding medium is useful since the larger weight of the balls will transfer extra impact energy to the powder particles. It has also been reported that the final constitution of the powder is dependent upon the size of the grinding medium used[15].

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It was suggested that smaller balls produce strong frictional action, which encourages the amorphous phase formation. In fact, it has been shown that "soft" milling conditions (small ball sizes, lower energies, and lower ball-to-powder ratios) appear to favour amorphization or metastable phase formation[20, 32-34].

It has been calculated that the highest collision energy can be acquired if balls with different diameters are employed for the milling process[15]. During the initial stages of milling, powder particles are adhered onto the surface of the grinding medium and cold welding takes place. This is advantageous for the grinding medium as it prevents excessive wear while milling and the contamination level is kept to a minimum. Powder sizes must be kept in mind as to prevent formation of heterogeneous final product. The shortcoming of the powder coating the grinding medium, is the difficulty in detaching the powders and therefore the grinded powder yield is low. Usage of different large and small size balls during milling will minimize the cold welding and reduce the amount of powder coating on the balls. However, there is no specific explanation given for the improved yield under these conditions, but could be due to the dissimilarity in sized balls producing a shearing force that may perhaps help in detaching the powder from the surface of the balls.

As for grinding balls of the same size in either a round or flat bottom vial has been shown to produce tracks. Consequently, the balls roll along a well-defined trajectory instead of hitting the end surfaces randomly. Therefore it is necessary to use several balls, generally a combination of smaller and larger balls to "randomize" the motion of the balls[35].

3.5.6 Ball-to-powder weight ratio

Charged ratio(CR) is sometimes referred to as ratio of the weight of the balls to powder (BPR) and this is an important variable in milling processes. Values as low as 1:1[36, 37] to as high as 220:1[14, 38, 39] have been used by many different investigators. The commonly used ratio is 10:1 for milling of powder in a small capacity mill such as a SPEX mill. When the milling process is carried out in a large scale capacity mill, for example an attritor, a higher BPR of 50:1 or even 100:1 is used.

With an increase of BPR, this increases the weight proportion of the balls, the number of collision per unit increases and subsequently more energy is transferred to the powder

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particles and so alloying occurs faster. When higher energy is generated and more heat is produced, this also causes an alternation in the constitution of the powder. Amorphous phase formed may even crystallize if the temperature is substantial.

"Soft" conditions (e.g., low BPR values, low speeds of rotation, etc.) of MA produce metastable phases whereas "hard" conditions produce the equilibrium phases.

3.5.7 Extent of filling the jug

Since alloying in the midst of the powder particles transpire(produced) due to the impact forces applied on them, it is essential that there is adequate space for the balls and the powder particles nudge around without restraint in the milling container. Therefore, the amount (ratio) of filling the vial among the powder and the balls is important. If the capacity of the balls and the powder is very small, then the production rate is very small. On the other hand, if the quantity is large, then there is not enough space for the balls to move around and so the energy of the collision is less. Thus, care has to be taken not to overfill the vial; generally about 50% of the jug space is left empty.

3.5.8 Milling atmosphere

Milling atmosphere can have a major effect on the contamination of the powder. Consequently, the powders are milled in containers that have been either evacuated or filled with an inert gas such as argon or helium. (Nitrogen has been instigated to react with metal powders and subsequently it cannot be used to avoid contamination during milling, unless one is keen on producing nitrides.) Commonly used for creating an ambient condition is high-purity argon as it will avoid oxidation and/or contamination of the powder. It has also been observed that oxidation can be generally prohibited or reduced in the presence of a nitrogen ambient. Nevertheless, this does not appear to be true when reactive powders such as titanium or its alloy powders are milled.

Loading and unloading of the powder into the vial is carried out inside atmosphere-controlled glove boxes. These glove boxes are frequently evacuated and refilled with

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argon gas. Some investigators have even conducted the milling operation in mills that have been placed inside evacuated glove boxes[14, 40].

Different atmospheres have been employed during milling for specific purposes. For example, nitrogen or ammonia atmospheres have been used to produce nitrides[41]. Hydrogen atmosphere was used to produce hydrides[42]. The existence of air in the vial has been shown to produce oxides and nitrides in the powder, especially if the powders are reactive in nature. Thus, care has to be taken to use an inert atmosphere during milling.

When Cr-Fe powder mixtures were milled in different types of atmosphere. The powder mixtures milled with an argon atmosphere, no amorphous phase was produced and Cr peaks remained in the X-ray diffraction pattern. On the other hand, when the powder mixtures were milled in either air containing argon or a nitrogen atmosphere, the powder became completely amorphous[15].

3.5.9 Process control agents

When the milled materials are ductile the powder particles get cold-welded to each other, due to the heavy plastic deformation experienced during milling. Alloying among powder particles can arise only when a balance is sustained between cold welding and fracturing of particles. A process control agent (PCA) (lubricant or surfactant) is introduced into the powder mixture during milling to reduce the effect of cold welding. The PCAs can be solids, liquids, or gases. They are mainly, but not necessarily, organic compounds, which function as surface-active agents. The PCA mechanism is that it absorbs on the surface of the powder particles and lessens cold welding between powder particles and therefore suppresses agglomeration. The surface-active agents adsorbed on particle surfaces impede with cold welding and lower the surface tension of the solid material. Since the energy required for the physical process of size reduction, E is given by [43]

$$E = \gamma \cdot \Delta S$$

Equation 3-2

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where γ is the specific surface energy and ΔS is the change of surface area, a reduction in surface energy results in the use of shorter milling times and/or generation of finer powders.

A wide range of PCAs have been used in practice at a level of about 1–5 wt% of the total powder charge. The most important of the PCAs comprises of stearic acid, hexane, methanol, and ethanol. A partial listing of the PCAs used in different investigations and their quantities is presented in Table 7. Additionally, other exotic PCAs such as sodium-1,2-bis-(dodecyl carbonyl)ethane-1-sulfonate, lithium-1,2-bis-dodecyloxy carbonyl sulfasuccinate, diodecyl dimethyl ammonium acetate (DDAA), didocyl dimethyl ammonium bromide (DDAB), trichlorotrifluoroethane and others such as polyethylene glycol, dodecane, ethyl acetate, oxalic acid, boric acid, borax, alumina and aluminum nitrate have also been used. The majority of these compounds crumble during milling, intermingle with the powder and form compounds, and these are integrated in the form of inclusions and/or dispersoids into the powder particles during milling. Thus hydrocarbons containing hydrogen and carbon, and carbohydrates containing hydrogen, carbon, and oxygen are likely to introduce carbon and/or oxygen into the powder particles, resulting in the formation of carbides and oxides, which are uniformly dispersed in the matrix. These are not necessarily harmful to the alloy system since they can contribute to dispersion strengthening of the material resulting in increased strength and higher hardness[44]. The hydrogen subsequently escapes as a gas or is absorbed into the metal lattice on heating or sintering. Even though hydrogen gas primarily serves as a surfactant and does not usually participate in the alloying process[15], some reports indicate that hydrogen acts as a catalyst for amorphous phase formation in titanium-rich alloys[45, 46]. It has also been reported that PCAs affect the final phase formation, changing the solid solubility levels[37], modifying the glass-forming range[37, 47, 48], and altering the contamination levels.

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Table 7 Process control agents (PCAs) and the quantities used in different investigations[15]

Process Control Agent	Chemical formula	Quantity
Benzene	$C_{28}H_{59}NO_2$	-
Didodecyl dimethyl ammoniu acetste (DDAA)	$C_{36}H_{75}NO_2$	1.5 wt %
Dihexadecyl dimethyl ammoniu acetste (DHDA)	$C_{36}H_{75}NO_2$	-
Dodecane	$CH_3(CH_2)_{10}CH_3$	-
Ethanol	C_2H_5OH	-
Ethyl acetate	$CH_3CO_2C_2H_5$	4 wt %
Ethylenebisdistearamide Nopcowax-22 DSP	$C_{2}H_3-2(C_{18}H_{36}ON)$	-
Graphite	C	2 wt %
Heptane	$CH_3(CH_2)_5CH_3$	0.5 wt %
Hexane	$CH_3(CH_2)_4CH_3$	0.5 wt %
Lithium-1,2-bi-dodecyloxy carbonyl sulfasuccinate	-	-
Methanol	CH_3OH	1-5 wt %
Octane	$CH_3(CH_2)_6CH_3$	1 wt %
Paraffin	-	-
Polyethylene glycol	$H(OCH_2CH_2)_nOH$	-
Silicon grease	-	-
Sodium chloride	NaCl	2 wt %
Sodium-1,2-bis(dodecyl carbonyl)ethane-1-sulfonate	-	-
Stearic acid	$CH_3(CH_2)_{16}COOH$	1 wt %
Tetrahydrofuran	-	-
Toluene	$C_6H_5CH_3$	5 wt %

The presence of air in the milling container or milling of the powders at very low temperatures (cryomilling) has also been shown to minimize welding, most probably due to the increased brittleness of the powder particles at such low temperatures[17, 49]. Metal powders (with an fcc structure) milled in a hydrogen atmosphere have been found to become brittle and not stick to themselves or the container; probably due to the formation of a hydride phase[15].

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The nature and quantity of the PCA used and the type of powder milled would determine the final size, shape, and purity of the powder particles. Use of a larger quantity of the PCA normally reduces the particle size by 2–3 orders of magnitude.

The choice of a PCA for milling depends on the nature of the powder being milled and the purity of the final product desired. The nature and amount of PCA used during milling determine the final powder particle size and powder yield. In fact, one way of determining the effectiveness of the PCA is to determine the powder yield after MA. If the powder yield is high, the PCA is effective. If the powder yield is not high, then either the amount of PCA used is not sufficient, or probably it is not the right PCA.

It should be realized that there is no universal PCA. The amount of the PCA is dependent upon the (a) cold welding characteristics of the powder particles, (b) chemical and thermal stability of the PCA, and (c) amount of the powder and grinding medium used. The powder particle size tends to increase if the weight proportion of the PCA to the powder is below a critical value, while above this value the particle size tends to decrease. One has to decide on a PCA by looking at the possible interactions between the metal and the components in the PCA.

3.5.10 Temperature of milling

The temperature of milling is one more vital parameter in concluding the constitution of the milled powder. Since diffusion processes are concerned in the formation of alloy phases irrespective of whether the final product phase is a solid solution, intermetallic, nanostructure, or an amorphous phase, it is usual that the temperature of milling will have a major impact in any alloy system.

There have been only a few investigations accounted where the temperature of milling has been deliberately varied[15, 50]. This was made by either dripping liquid nitrogen on the milling container to lower the temperature or electrically heating the milling vial to increase the temperature of milling. These investigations were undertaken to study the effect of milling temperature on the variation in solid solubility levels, or to determine whether an amorphous phase or a nanocrystalline structure forms at different temperatures. During the formation of nanocrystals, it was reported that the root mean

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square (rms) strain in the material was lower and the grain size larger for materials milled at higher temperatures[51]. The extent of solid solubility was reported to decrease at higher milling temperatures.

Formation of an amorphous phase by Mechanical Milling(MM) occurs by a different mechanism than during Mechanical Alloying(MA). The increase in free energy of the crystalline phase by the introduction of defects such as anti-site chemical disorder or increased grain boundary area through formation of a nanocrystalline structure is considered responsible for amorphization during MM. Thus, lower milling temperatures are expected to favour amorphization. However, both increased and decreased kinetics have been reported. Shortened milling times for amorphization were reported for milling of NiTi at 170°C than at 60°C[15].

3.6 Powder Properties

Inorder to achieve the correct distinctive requirements for an implant it is important to consider characteristics of the powder such as: particle size, and size distribution, particle shape, structure and surface condition[52].

3.6.1 Size

Particle size varies with particle shape as well as the techniques by which the powder was manufactured. Figure 3 give a variation of particle shape with particle size. A particle size analysis, which assumes a constant shape, could potentially have a large error. The simplest type of analysis will be to have a simple quantitative shape descriptor proving adequate information. The most direct analysis type would be the aspect ratio. Aspect ratio is defined as the maximum particle dimension divided by the minimum one. An example of sphere count with aspect ratio is unity, while for ligament type particles a value of 3 counts is most likely due to the shape of the powder. Flake particles can have an aspect ratio in excess of ten and in some instances it can be as high as 200.

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Figure 3 Variation in particle shape with particle size[53].

Particles sizes and shape are a concern when sintering metallic powder. As normal sintering is conducted using a powder compact, e.g. pellets made from powders. Particles are mostly packed in non-order arrangements and random packing density of uniform spheres is reported to vary from 56 to 67%[54]. Smaller particles when introduced will distribute themselves in the interstices of the larger particles. Therefore the packing density, porosity and pore size decrease. The distribution of particles size affects the packing density, D , (See Figure 4[55]). When mean particle size is below 100 μm , there is increased interparticle friction, and particles bridging is more likely to occur. When lower packing density is a result of using smaller particles, an increase in surface area with a corresponding increased resistance to compaction. The greater significance of short-range weak force such as those controlled by the electrostatic field, moisture and surface adsorption. Since interparticle cohesion increases with a decrease in size, there is an increase in agglomeration and poorer packing for decreasing particle size[56].

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Figure 4 Effect of particle size distribution on the green density of the compact[55].

Particle shape and surface roughness can also affect the interparticle friction bridging of particles and hence the packing density. Packing density will decrease as the shape departs from equiaxed (spherical) for similarly sized powders. Green density improves as the roughness of particle surface decreases. With use of equipment such a vibrator bowl or lubricants, they can assist in attaining a high packing density. Other problems may rise from agglomeration and/or size segregation.

In a study conducted by Ik-Hyun Oh[57] of sintering with various powder sizes of titanium powder with the following different production method of the powder:

- 300-500 μm plasma rotating electrode process (PREP)
- 150-250 μm gas atomisation
- 45-150 μm gas atomisation

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Reviewing the following Ti compacts sintered at 1573 K with 374 μ m powder (a) and at 1373 K with gas atomized 65 μ m powder (b). The surfaces of porous Ti compacts were observed to be roughened by pore formation, and contained a considerable numbers of pores. Neck formation between Ti powder particles was observed in the porous compact sintered at 1373 K with 65 μ m powder (Figure 5b). On the other hand, only contacts between Ti powder particles were observed in the compact sintered at 1573 K with 374 μ m powder in spite of higher sintering temperature (Figure 5a). This could be attributed to the surface energy per unit volume, which depends on the inverse of the particle diameter. Thus, smaller particles with high specific surface area have higher energy, so that they could be sintered faster in spite of lower sintering temperature. Surface roughness values of porous Ti compacts sintered at 1573 K with 374 μ m and at 1373 K with 65 μ m were 33.7 and 9.3 μ m, respectively.

Figure 5 SEM micrographs of porous Ti compacts sintered at (a) 1573 K with 374 μ m powder and (b) 1373 K with 65 μ m powder[57].

Sintered materials have been synthesised with mechanically alloyed powders. Intense attrition milling can generate metastable powders and these metastable structures can be preserved during sintering. It is desirable to have powders with reversible agglomeration and deagglomeration characteristics to regulate packing, handling and sintering behaviour. Superplastic forming is practicable with nanocrystalline materials and is more favourable in some cases to pressureless sintering because of microstructure control.

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Research on grain growth during sintering for submicron size powders is still lacking. In the attendance of liquid phase little information is available. The challenge here is to extend the knowledge available for large particles sintering to the small sized one.

3.6.2 Shape

Shape of the particles is a distributed parameter that can influence the packing, flow and compressibility of a powder. Particles shape provides information on the powder fabrication route and helps explain many processing characteristics. As it is relatively difficult to quantify particle shape, qualitative descriptor are typically used. Figure 6 gives a collection of particle shapes and shows the appropriate qualitative descriptors. Microscopy techniques are the most appropriate for quantifying shape.

Figure 6 Collection of possible particles shapes and qualitative descriptors[53].

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3.6.3 Compressibility

In most powder metallurgy applications, good packing characteristics are desired. Loose packing of powders gives a low apparent density and form pores after sintering. High packing densities are achieved by adjustment of particle size, shape and size distribution. Coordination number is the number of touching neighbours that any particles has in a powder ensemble, and is synonymous with the number of nearest neighbours. Fine particles will lead to an increase of interparticle friction, giving a lower number of nearest neighbours. Thus the finer the mean particles size, the lower the apparent density. The relation between coordination number and packing density is shown in Figure 7 for regular and random packing.

Jernot et al[53] recent analysis of spheres showed that the apparent density (when expressed on fractional basis) related to the coordination number N_c as follows[43]:

$$\rho = (N_c - 1 / N_c)^3 \quad \text{Equation 3-3}$$

where ρ is the fractional density.

Particle size effects are generally tied to the surface area. Finer particles sizes imply higher interparticle friction and therefore lower packing densities. An irregular particle shape will hinder packing due to an increase of surface area.

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Figure 7 Various relations between packing coordination and fractional density for equal sized sphere[53].

3.6.4 Density & Interparticles Friction

The density or packing properties decrease because of poor flow past neighbouring particles. Apparent density of powder is the density (mass/volume) when the powder is in the loose state without agitation, this is known as *bulk density*. *Tap density* is the highest density, which can be achieved by vibration of powder without the application of external pressure. The theoretical density when there is no porosity present. The angle of repose is another friction index. It is the angle formed during pouring of powder into a pile as shown in Figure 8 where the tangent of α equal the height divided by the radius of the loosen powder.

Two common devices are used for measuring the apparent density. They are the:

- Hall Flowmeter(Figure 9) used for coarser particles; both flowrate and apparent density are measured by this device, and

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- Scott Volumeter device (Figure 9) applied for fine refractory powders, which have higher interparticle friction.

Figure 8 Angle of repose is a measure of the interparticle friction[53].

Figure 9 Hall Flowmeter and Scott Volumeter Device[53].

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3.6.5 Alloying Elements

Alloying elements were deemed to enhance the properties of the material to meet demand in engineering purpose for any application. For the development of a biomaterial it requires certain properties such as enhancing the bulk modulus. The influence of solid solution for different alloying elements on the bulk modulus was studied by Guo[58]. From Figure 10 it is clear that elements such as V, Cr, Mn, Fe and Co increase the bulk modulus. The increment ranges from 7.4% to 23% for the β -Ti and is about 2.5% for the α -Ti. The actual effect of Ni and Cu on Young's modulus appears to vary with the structure of the solid solution. Alloying with either Ni or Cu enhances the bulk modulus of the β -Ti but reduces the α -Ti. For 4d- and 5d-transition metals, Zr, Nb, Mo, Hf, and Ta marked the reduction of bulk modulus of both the α -Ti and β -Ti. The alloying atom, Al, Si, Ga or Sn, evidently enhances the bulk modulus of β -Ti, but only gives rise to a weak effect on the modulus of α -Ti. The rare-earth atom, Sc, reduces the bulk moduli of both structures[58].

Figure 10. The effects of various alloy elements on the relative bulk modulus of binary Ti-X alloys[58].

In another study conducted by Guo[59] of the titanium computational alloying with a variety of elements was to investigate the relative strength and modulus of β -type bio-titanium alloys. There was a concern that several of the materials still suffer from a large

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degree of biomechanical incompatibility, due to their relatively high elastic modulus (about 120 GPa), compared to a bone of max. 30 GPa)[60]. Several materials had their strength and modulus calculated mathematically and these are reported in Table 8.

Table 8 Calculated strength and modulus of some Ti-M alloy[60]

Alloying atom	Strength (MPa)		Modulus (GPa)	
	σ^I	σ^{II}	μ^I	μ^{II}
Ti	2228	2168	132.34	132.46
V	2422	2290	137.18	137.86
Cr	2530	2392	137.56	140.12
Mn	2592	2390	124.86	142.58
Fe	2374	2368	130.76	142.68
Zr	1932	1898	125.02	116.40
Nb	2262	2110	142.64	128.32
Mo	2480	2232	151.88	135.58
W	2436	2092	157.82	133.68
Ta	2232	2000	146.40	127.86

Among the elements studied, the relative strength of Ti-M alloys to unalloyed β -Ti, σ_M/σ_{Ti} , is larger than unity if the relative concentration of an alloying element is about 7 at.% (except for Zr), which is the case for V, Cr, Mn, Fe and Mo. However, it is smaller than unity for Zr, Nb, W and Ta, when the relative concentration of the alloying element is about 4 at.%.

Figure 11 Relative strength of Ti-M alloys to the β -Ti [60]

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Figure 12 Relative modulus of Ti-M alloys to the β-Ti[60]

Figure 13 Relative admissible strain (ratio of the strength to elastic modulus) obtained from the calculation[60].

As for the alloy-design point of biomedical applications, it has been identified that the suitable alloying element should be Nb, Mo, Zr, and Ta, with due consideration of the biocompatibility of the element. The ideal material should possess good strength, high fatigue resistance, and a low elastic modulus. By mechanical alloying the cluster II and I with suitable at. % of the elements relative high strength, good strain and low modulus can be obtained (See Figure 11 to Figure 13).

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3.6.6 Impurities

Elemental powder are subdivided into two groups:

- Relatively high-purity material where chemical analysis focuses on the impurity concentration and,
- Prealloyed powder constitute micro-casting with multiple elements in a predetermined ratio and impurity concentrations.

Bulk chemical information is often required to understand the surface condition of the powder. This concerns the oxides, adsorbed organic films and the presence of the surface coating like silica. It is important to differentiate between the absorption of oxygen, moisture and oxides to determine the appropriate cleaning treatments. A loss on reduction is reported to show the weight loss when heated in hydrogen environment at low temperatures. This represents a measure of surface oxidation.

For some materials, the powder hardness provides a gross gauge of the impurity level and assures that the powder has been annealed. The elemental powders are often derived either from ores or metal scraps. The ore based elemental powder will usually have less lot-to-lot chemistry variations than the scrap based powders. At the same time, ore based powder tend to have higher inert or oxide inclusion contents. Powder fabricated by fusion based techniques provide greater opportunity for chemical refining and can be expected to be of higher purity.

Bulk chemical characterization of powder can be obtained from:

- Emission spectroscopy
- Calorimetry
- X-ray fluorescence
- Neutron activation analysis

X-ray fluorescence is the most suitable analysis technique and has a lower sensitivity of approximately 10ppm. Advanced techniques are capable of extending analytical accuracy to 0.01ppm level. Microanalysis by electron or ion beam is useful for the chemical composition in small volume. It is not useful as a form of routine analysis since they are typically semi-quantitative and slow[15, 39].

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Pre-alloyed powder should be checked to verify adherence to chemical tolerance. These powders tend to have higher oxide surface concentration. In the cases involving premixed powder blends, the blend chemistry should be checked and reblending and deagglomeration should assure blend uniformity.

Contamination of the powder can be traced by[15]:

- Chemical purity of starting powder
- Milling atmosphere
- Milling equipment (jugs and grinding medium) and
- Process control agent added to the powder

Possible sources of contamination can be

- Substitutional or interstitial in nature, while contamination from source (supplier or ore)
- Interstitial in nature and that from
- Mainly substitutional, though carbon from steel milling equipment can be interstitial impurity

Interstitial contamination was reported by of Godfrey et al[61] while working on Ti6Al4V, the initial powder contained 1050ppm of oxygen and 120ppm of nitrogen produced by gas atomised powders. For the titanium powder as received had a level of 1130ppm of oxygen and 120ppm nitrogen. When the powders were mixed and the milling process was carried out on the powder the contamination was limited to 65ppm of nitrogen[61].

3.7 Fundamentals of Mechanical Testing

Mechanical testing is executed to verify the response of material of construction, components of fabricated assemblies or by other manufacturing processes when subjected to load or deformation.

Mechanical properties distinguish and are employed to portray in quantitative manner the inborn mechanical behaviour of the material. Properties used in design to size

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components are in almost all instances assumed to be uninfluenced by geometrical considerations such as size and shape. The stress (for example, the applied load divided by the area on which the load acts) required to break a tensile specimen is the same for all tensile specimens of an alloy provided that the metallurgical structure is the same; whereas the inclusion prevents materials from meeting a strength or ductility requirement. In such cases, non-destructive testing (NDT), such as radiography or ultrasonic, provides an important tool to check minimum guaranteed behaviour. Similarly, the presence of quench cracks may be determined by penetrate-dye or magnetic particle inspection. Sometimes, NDT procedures are used to directly measure mechanical properties such as those defining certain stress-strain relationship, i.e. tensile modulus, shear modulus and Poisson's ratio.

An important aspect of mechanical testing is recognition of aspects of mechanical behaviour that may not be revealed by standardised tests and knowledge of whether a property determined from a test is truly a property describing the inherent behaviour of the material. Mechanical testing, tests the properties of the material as in as received stock or as material removed from the fabrication and manufacturing processes. It provides both quality control and quality assurance.

3.7.1 Compressive Testing

Compression testing is a method for assessing the ability of a material to withstand compressive loads. This test is commonly used as a simple measure of workability of metal, particularly in forging and similar bulk deformation processes. Engine mounts, bolster springs, cast products, and similar components are tested to determine load versus displacement.

Both concepts of uniaxial and compressive loading are quite similar. Strain is produced parallel to the applied load that has the same sign as the applied load and two transverse strains are produced that are opposite in sign to the applied load. Below the proportional limit, the strain in the load direction, in both cases, can be calculated using a single value of Young's modulus. Transverse strain can be calculate using a second material constant, Poission's ratio (ν):

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$$\Sigma_y = \Sigma_z = v_{\Sigma x} \quad \text{Equation 3-4}$$

$$V_{\text{transverses}} = v_{\text{axial}} \quad \text{Equation 3-5}$$

Compression testing to obtain mechanical properties however, is performed with less ease than tensile testing. Similar to tensile testing, compression testing is used to obtain properties used for elastic design, but in addition, it is used to obtain properties that predict plastic formability. Compression testing presents considerable experimental difficulty in contrast to tensile testing, due to crack formation increasing the probability of opening up and also due to the presence of the action of tensile stress. The failure of a ductile material in compression is not characterized by the formation of a neck or by an abrupt rupture of the specimen into two pieces. (Cracks may form, but they are internal and not visible unless the specimen is sectioned.) This leads to a question of whether an ultimate stress analogous to the UTS can be defined for compression loading. Brittle cylindrical specimens loaded in compression fail in shear on a plane inclined to the load, and therefore, do actually break into two or more pieces. In this case, an ultimate stress can be defined.

In addition to the question of what constitutes failure in compression testing, there are other difficulties encountered in conducting the test and interpretation of the experimental data. For example, maintaining complete axially of the applied load is important. In tensile testing, self-aligning grips make this relatively simple to accomplish. In compression testing, if the specimen is tall in comparison to its diameter, this can present a major difficulty. Nonaxiality of the load induces a bending load in the specimen, in addition to the axial load, that will cause buckling if it becomes large. Alignment of the loading platens to impose strict uniaxial loading is easier if the specimen contact area is large, but this introduces other difficulties.

Friction forces exist at the specimen-platen interfaces that tend to restrict the increase in diameter of the specimen as it decrease in height. These forces are of magnitude μP where μ is the coefficient of friction and P is the compressive load. Due to these friction forces, loading on the specimen is not uniaxial. The effect of these fraction forces is two-fold; (1) an analysis indicates that the magnitude of the applied stress is increased over

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what it would be if the specimen were loaded uniaxially (i.e., the situation if μ equal 0), and (2) diameter expansion is hindered near platens, but not in material well removed from the platen, so that the specimen becomes barrel shape Figure 14.

Figure 14 Elastically loaded region and barrelling in a compression specimen for two different height to width ratio

Because of the increased magnitude of the applied stress, deformation at mid-height is plastic; while it is still elastic near the specimen-platen interface. The ratio of the elastically strained material to the plastically, strained material increase as the specimen height decreases, so that barrelling increase during the course of a test. The unfortunate consequence is that specimens selected show extensive barrelling and for which the internal stresses in the material have a large biaxial component. Therefore, some compromise must be made in selecting specimen dimensions. A height-to-diameter ratio of about 3 to 1 often is selected to minimize buckling that occurs due to the bending loads generated by nonaxial alignment of the load. Because of the increasing contact area and the elastically strained material near the platen, the load deflection curve bends upwards as the specimen decrease in height Figure 14. A dramatic increase in load occurs if the elastically strained regions of Figure 14 overlap.

Due to the presence of frictional forces, the pressure distribution across the specimen is not uniform, as shown in Figure 15 and Figure 16. The pressure distribution is given by:

$$P = \sigma_0 \exp [(2 \mu/h)(r-x)] \quad \text{Equation 3-6}$$

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Where p is pressure, δ is yield stress, μ is coefficient of friction, r is cylinder radius, x is distance from centre of cylinder to data point on x-axis, and h is cylinder height.

Two useful calculations for compressive strength and modulus are:

Compressive Strength = maximum compress load/minimum cross-section area

Equation 3-7

Compressive Modulus = change in stress/ change in strain

Equation 3-8

Figure 15 Curves illustrating the relationship of compression load to height reduction for various d_0/h_0 ratios[62]

Figure 16 Replot of curves to extrapolate curves to d_0/h_0 equals 0 d_0 is initial diameter h_0 is initial height[62]

Figure 17 also shows how the pressure distribution changes as the height decreases and as the coefficient of friction changes. The load needed to deform a cylinder can be estimated by multiplying the average pressure on the specimen by the contact area. Figure 17 indicates that the load required to deform materials becomes greater and also, increase with a rise in the coefficient of friction. Without overload protection on the load cell, precautions must be taken so that the large loads required to cause plastic flow do not damage the load cell by exceeding its capacity, especially at large plastic strains characteristic of forming processes.

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Coefficients of friction are kept as low as possible to minimize barrelling and the development of large loads by providing lubrication at the platen-specimen interface. Two possibilities are the use of lubricating oil and oil grooves in the specimen or platen, or thin Teflon (trademark of DuPont) sheet between the platen and specimen.

If testing is to be done in accordance with ASTM specifications, the procedures are defined in E9 [62](room temperature testing) and E209[62] (elevated temperature testing). Specification E9 provides for three standard specimen geometries with length to diameter ratios of between 0.8 to 1 and 10 to 1. The lowest ratio is used to test thin materials loaded normal to the thin surface, such as bearings; the medium ration are used for general testing of metallic materials; and the longest specimens are used to determine the elastic modulus of metallic materials. Because of the possibility of buckling due to a large slenderness ratio (length to diameter), the long specimens must be supported in a guided jig. Several such jigs are shown in ASTM E8[62].

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Figure 17 Pressure distribution across a specimen loaded in compression at different height reductions and for different coefficients of friction[62]

In a study by Bram et al.[63] sintering of porous titanium with the use of Carbamide (urea) particles of spherical or angular in shape and ammonium hydrogen carbonate particles of angular shapes were used as spacer-holder materials. Bram et al. was able to create with apparent porosity 7, 60 and 80% thus making porous Titanium. When compression test carried on the porous sintered Titanium, at the first stage an almost linear increase in the compressive stress was observed. An area change followed by the increase with small changes in compressive stress. When using higher upsetting rates, a further increase in the stress is expected with respect to the complete consolidation of the porous structure. In this case a plastic deformation of the almost-dense microstructure occurs. Highly porous titanium seems to be a good candidate for energy absorption application. As porosity dropped from 77 to 60% causing the compression curve to shift

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by a factor of 10 into a higher stresses. A distinct increase is observed when porosity was reduced to 7%.

Figure 18 Compressive-stress curves of Titanium samples with different porosities.[63]

3.8 Porosity Testing

One major influence on the mechanical properties of a material is the degree of porosity. Over the years, a wider variety of technology has had be developed in characterizing porous materials ranging from straightforward Archimedes' principle to difficult to use equipment like micro tomography can be use in porosity measurements. This section will discuss the technical respective application and limitation of the equipment. Porous material can be characterised using a wide range of techniques:

- Density measurement
- X-ray radiography and radioscopy
- X-ray computed tomography
- Eddy-current sensing
- Acoustic measurement
- Vibrational analysis
- Porosimetry and permeametry

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- Electrical and thermal conductivity measurement

These various methods of characterising the porosity will be briefly discussed in this section.

3.8.1 Density measurement

Finding the weight of the sample and measuring its volume using Archimedes' principle can determine the overall density of the porous material. Like measuring the buoyancy in a liquid with a known density. If the sample characterised does not have a closed outer skin, penetration of the liquid into the pores has to be prevented by coating its surface (for example with a polymer film).

3.8.2 X-ray radiography and radioscopy

Porous materials can be mapped by simple X-ray absorption techniques (transmission radiography). An X-ray beam is directed through a sample and its attenuation is measured. One averages over a certain lateral area and scans over two dimensions, thus obtaining a 2D absorption map of the porous material. The method yields an integrated signal along the direction of the beam, i.e. the attenuation is related to the total mass in a column of material. If thin slices of porous sample are investigated, i.e. pieces with a thickness in the order of the average pore diameter one can resolve individual pores and map the true pore morphology. However, if the slices are much thicker, single pores are not further distinguishable. Even features such as big pores or holes of a size of one fourth of the thickness of the foam cannot be resolved properly in some cases[64]. Figure 19 shows inhomogeneous porous lead in transmission. Some of the very large pores can be seen, but it is impossible to resolve most of the small pores because many pore images are superimposed on each other. Materials of relative thin thickness and low densities, are more favourable as the penetration power of the X-ray is high, therefore mapping in more details of what's beneath the surface of the porous material. With the advancement of the technology, creation of metal foams of 4–10 mm thickness, the features porosity could be observed in real time by using synchrotron radioscopy [65]. Up to 3 images with 40µm

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resolution were obtained per second and, e.g., individual cell walls could be captured as they were formed.

Figure 19 Image of a lead foam obtained by X-ray transmission radiography[64]

3.8.3 X-ray computed tomography

Three-dimensional density distributions can be obtained by means of computed X-ray tomography (CT)[66]. X-ray images of a sample are taken from a large number of directions, usually by rotating and translating the source and the detector around the sample (spiral scanning, see Figure 20). From the various images obtained the attenuation of the rays at any point of the object and therefore the local density are reconstructed mathematically[67]. Figure 21 shows a high resolution image of a porous zinc material obtained by this method. The sample shown is about $5\text{mm} \times 5\text{mm} \times 5\text{mm}$ large, with a spatial resolution of $5\mu\text{m}$. A synchrotron generated X-ray beam (52 keV) was used for obtaining this image which even resolves the internal surface structure of the cell walls. Medical or technical tomographs are typically more limited in resolution yielding about 0.7 or 0.1 mm, respectively. This lower resolution, however, is sufficient for quality control of cellular components in most cases because for obtaining 3D density distributions the CT raw data is averaged over rather relatively 3D volume elements anyway. The choice of the size of these elements depends on the information desired. If one wants merely to detect hard and soft regions in the foam, the averaging volume is of the order of an average cell volume, i.e. in the range of millimetres [64].

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Figure 20 Experimental set-up in X-ray computed tomography

Figure 21 High resolution 3D-image of a zinc foam obtained by computed tomography[68].

Nuclear magnetic resonance tomography, a valuable tool in scanning human bodies, is not suited for investigating metallic structures because the penetration depth of the stimulating rf field is very small for the frequencies usually applied (for aluminium, $11 \text{ MHz} \times \text{magnetic induction of field in tesla}$).

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3.8.4 Eddy-current sensing

Porous samples can be characterised by their relative density and pore size by carrying out multifrequency electrical impedance measurements[69]. This can be achieved by using an excitation coil that produces an alternating magnetic field. Induction effects of the eddy currents, this causes a corresponding magnetic field around the metal foam sample, which can then be picked up with a secondary coil. The eddy currents not only depends on some geometrical factors and frequency, but also on porosity properties within the material. It can be shown that porosity has a marked effect on the output signal. Therefore, this method can be utilized to measure local densities and other pore parameters in a sample after appropriate calibration.

3.8.5 Acoustic measurement

The sound absorption properties of porous media are usually measured in an impedance tube, which allows for quick and precise measurements. However, as only perpendicular incidence of the sound wave on a sample can be characterised, further tests have to be carried out before a newly developed sound absorber can be used. The impedance tube contains the disk-shaped sample near one end with a variable distance to the rear wall and a sound emitter and detector at the opposite end[64]. For the usual acoustic frequency range tubes of about 60 cm length and 30 or 100 mm diameter are used for high (≥ 0.8) kHz, and low frequencies (≤ 1.6 kHz), respectively. Normally one measures the attenuation as a function of frequency. If the cavity between sample and rear wall is also varied, one obtains a series of functions $\alpha(v)$, absorption coefficient versus frequency. If the samples have interconnected pores, the absorption curves are shifted to lower frequencies when the cavity is enlarged. Dense samples and porous samples with closed pores, however, have the same absorption curve independent of the cavity because sound cannot penetrate the sample and the absorption takes place on its surface. It is necessary to carry out measurements on more than one sample, particularly for small tube diameters, and it is useful to make two measurements for each sample, each one for one possible orientation of its sides. The surface dominated absorption of closed cell foams is clearly different for the two orientations; whereas the volume dominated absorption of open structures remains unchanged when the sample is flipped.

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3.8.6 Vibrational analysis

Young's modulus and the hollow part materials can be determined by vibrational analysis. In the simplest technique, a long bar of rectangular or round cross-section or a thin quadratic plate made of the material is forced into vibrations. Longitudinal, transverse or torsional excitations can be created. The sample can be clamped at one or two ends, or be supported by or suspended from thin wires. The sample can be excited by magnetic fields and the resulting vibrations can be picked up by an impedance coil. Another possibility is to fix the sample directly to an electromagnetic shaker to avoid clamping[70]. The amplitude of vibrations as a function of excitation frequency shows characteristic resonance peaks. The positions of the peaks ν_p allow one to calculate Young's modulus E from the sample dimensions and mass using standard formulae. The widths $\Delta \nu/\nu_p$ of the resonance peaks define the loss factor η [64]. Measuring the properties of cellular materials, however, is not trivial. The materials are often inhomogeneous with an unknown mass distribution. The effective (average) Young's modulus obtained from the resonance frequencies for such an inhomogeneous material then depends on the mass distribution. In measuring the loss factor, one has to suppress the influence of parasitic losses from the sample support. Using clamps, one introduces friction between clamps and samples, whereas supporting a foam bar on thin wires creates problems because the location of the vibrational nodes of the inhomogeneous sample is unknown[68].

3.8.7 Porosimetry and permeametry

Dealing with porous metallic materials with open pores one is interested in determining parameters associated to the internal structure: specific surface area, pore size distributions and channel size distributions. Various methods are currently in use:

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Mercury porosimetry.

It is based on the intrusion and extrusion of mercury into the pore volume under pressure. The intruded volume and pressure data are related to the size of the cells. However, pores smaller than a few hundred microns are hard to detect.

Gas absorption techniques (BET).

This instrument is used to measure the specific surface area (units of m^2/gram) and the distribution of pore sizes in samples by gas absorption techniques. Surface areas in the range from $0.1 \text{ m}^2/\text{g}$ and higher can be measured by using nitrogen gas whereas the use of krypton permits measurements of solids with very low surface areas of about $0.001 \text{ m}^2/\text{g}$. Pore diameter analysis in the range of 15 to $5,000 \text{ \AA}$ [71] is possible. They allow for a fairly accurate determination of the total internal surface area of a cellular material. Even very small pores down to an atomic scale can be detected. Chemisorption of other gases such as carbon dioxide is also possible.

Permeametry.

It is based on the study of a gas or liquid flow through a porous medium. One measures the pressure drop Δp along a foam column of height s as a function of mean fluid velocity v and finds a linear relationship for very slow flow (Darcy's law for flows dominated by viscous forces) and a quadratic dependence for higher flow rates (Forchheimer law) when energy losses due to the inertia of the flowing fluid become important. Some results for a gas flow through various open-cell aluminium samples are shown in Figure 22. By knowing the viscosity of the fluid, a permeability and a friction coefficient can be derived. Assuming that the friction is related to the internal surface area of the pore volume, an estimate can be obtained for the specific surface area. The values obtained this way are lower than the ones from BET measurements because only a part of the internal surface interacts with the flowing fluid[72].

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Figure 22 Pressure drop measurements on various open-cell materials[64]

3.8.8 Electrical and thermal conductivity measurement

Measurements of the electrical resistivity are fairly straightforward. Owing to the low resistivity of metallic materials a small cross-section is desirable. However, the finite cell size imposes a minimum on the cross-section. A good contact between the leads and the foam has to be ensured. For aluminium foams, with average pore diameters of about 2 mm, rectangular specimens with a cross-section of 200 mm² and 200 mm length have been used. The measurements were carried out in the four-point mode with copper contact plates clamped to the foam[64].

After comprehending the powder manufacturing methods, powder handling and processing techniques as well as mechanical properties the material and characterisation of porous materials. The next choice of discussion will be the sintering and transient liquid phase sintering.

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4 Sintering of Porous Materials

4.1 Compacting

Compaction relies on an external source of pressure for deforming the powders into high-density mass, while providing shape and dimensional control to the powder. Delivering this pressure to the powder involves particles rearrangement, deformation and possible compacting it. The mechanical constraints and the rate of pressurization are the main process parameters, which determine the results densities.

4.1.1 Green body and Particle Bonding

Application of pressure can amplify the density and strength of green compacts. Externally applied pressure domino effects in repacking and deforming of the particles into higher density form. Particles coordination of compact increases as the contact area within particles, this lead to increasingly deformed and enlarged contacting area. Compaction is not a reversible process while the applied pressure modifies shape and size. Due to the dramatic increase in interparticle bond strength connected with increased compaction, contacting points between particles increase, flatten and grow to form a planar contact surface. Green compact depends directly on the properties of the material's yield strength, hardness and strain hardening. Particles with lower hardness, strength or strain hardening rate allow a higher degree of compaction. Therefore larger particles produce a higher packing density and exhibit higher densities at all compaction pressures. When compacting smaller particles it becomes increasingly difficult and harder to compact with an increase in number of contacts points higher strain hardening rate and higher stress concentrations[73].

The pressure distribution along the length of the compact is determined using the slab method of analysis of deformation process.

Let D be the diameter of the compact, L its length, and p_0 the pressure applied by the punch.

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The below Equation 4-1 shows an element dx thick with the relevant stresses: the compacting pressure p_x , die-wall pressure σ_x , and the frictional stress $\mu\sigma_x$.

Balancing the vertical forces and simplifying, one gets[74]:

$$D dp_x + 4\mu\sigma_x dx = 0 \quad \text{Equation 4-1}$$

We introduce a measure k of the interparticle friction during compaction. We get a relationship between p_x and σ_x :

$$\sigma_x = k p_x \quad \text{Equation 4-2}$$

$k = 1$ when there is no friction between the particles. In this case, the powder behaves like a fluid, i.e., we have a state of hydrostatic pressure.

Substituting for σ_x in the first equation, we get an ordinary differential equation in p_x . Integrating, we get:

$$p_x = p_0 e^{(-4\mu k x / D)} \quad \text{Equation 4-3}$$

Thus the pressure within the compact decays as the coefficient of friction, the parameter k , and the length-to-diameter ratio increase.

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Figure 23 Reduction of Pore Size

A possible model of changes in pore profile is proposed and illustrated in Figure 23. Before pressing the powder particle surfaces are not deformed and, to simplify the problem, all the pores are assumed to be similar and near-globose (Figure 23 (a)). During pressing, due to both the great affinity of Ti with oxygen[75-77] and work hardening from the ball-milling technique used before pressing[78], the blended powder is hard and more easily deformed by shearing rather than by pressing as the pressing pressure is low. At the same time, the friction between the die wall and the powder particles also causes greater deformation in those particle surfaces perpendicular to the axial direction and, as a result, the pores in the green compact appear elliptical with their longer axes parallel to the axial direction (Figure 23(b)). However, the more the particle surface deform during

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pressing, the less will it shrink during the sintering stage due to release of the deformed stress[77]. Therefore, the shrinkage will be of greater value in the axial rather than in the radial direction (Figure 23(c)), and the R/A -ratio will be less than 1.

4.1.2 Porosity

A direct relationship exists between particles size and the pore size observed in the green body. Large particles tend to pack inefficiently, leading to large pore sizes. These pores are found to remain during sintering, thus reducing the strength of the final product. General porosity means the fraction of pore volume to the total volume. It can be defined as[8]:

$$P = (1 - \rho / \rho_0) \times 100\% \quad \text{Equation 4-4}$$

Where ρ is the density of porous material, ρ_0 is the density of corresponding bulk material.

Open porosity ratio (η) is the ratio of open porosity (P_1) to general porosity:

$$\eta = (P_1 / P) \times 100\% \quad \text{Equation 4-5}$$

Packing can be improved by reducing the particles sizes. When small particles present in these powders will fill the voids between the larger particles, thus reducing the overall pore size. Finally, the presence of large agglomerates must be avoided as these can lead to defect formation during sintering, as agglomerated grains tends to grow more quickly than well-dispersed particles. Again reducing the strength of the final product. See Figure 24 for illustration of an open and close pore.

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Figure 24 Schematic illustration of pores for a porous material[8].

After compacting the powder, the pores formed are open and interconnected but after sintering both open and closed pores exist[79] (See Figure 25). Note that there is no dramatic shift when the pores become closed as an indication of final sintering stage. These closed pores form as the tubelike pores encountered in the intermediate-stage sintering become unstable. A calculation of the instability of a cylindrical pore of length l and diameter d_p gives[79]

$$l \geq d_p \pi \quad \text{Equation 4-6}$$

as the condition for breakdown. Grain growth elongates the pores, increasing the length l , while densification reduces the diameter d_p , resulting in a natural breakup into discrete pores. Ideally, for a pore geometry of cylinders occupying grain edges, instability occurs at a porosity of approximately 8%. Since there is a distribution in grain shape, grain sizes, most materials exhibit a range of porosities over which pores collapse. Normally, pores start to close at about 15% porosity and are all closed by 5% porosity. If the grain boundary energy is ignored, the resulting pores are spheroidized through surface transport processes, with a final diameter equal to 1.88 times the initial cylinder diameter[77]. Note that the diameter of the pore with conversion into a sphere during the onset of final-stage sintering.

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Figure 25 Variation of open and close pores fraction versus the total porosity for urania sintering at 1400°C[79].

4.1.3 Compaction Effects

Particles sizes have a large effect on the interparticle friction, packing density and pore size. Finer particle sizes are more difficult to press, since large pores collapse under lower pressure than finer pore. Therefore, rate of densification with pressurization is greater for coarser particle sizes. Particles having internal porosity (sponge powder) are difficult to compact as during the initial compaction there is total collapses of the larger interparticle pore. Sponge powder shows a high initial compressibility but resist compaction to high final densities.

These factors that impair the compressibility also degrade the green strength. Other characteristics improve the compressibility as well as the green strength. Finer particle size is an extrinsic characteristic that hinders compaction. Due to lower pressed density, fine particle size results in a decreased green strength (or unless increase in compaction pressure). Irregular powder yields a higher green density because of the mechanical interlock. Spherical powder exhibit high initial packing densities, but not the strength. Particles size effect becomes more apparent as the particle shape become less regular.

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4.1.4 Density

An important parameter is the apparent density (AD) of the powder, i.e. the mass of a given volume, since this strongly influences the strength of the compact obtained on pressing. AD is a function of particle shape and the degree of porosity of the particles. For the choice of powder characteristics is normally based on compromise, since many of the factors are in direct opposition to each other. An increase in the irregularity and porous texture of the powder grain, i.e. decrease in apparent density, increases the reduction in volume that occurs on pressing and thus the degree of cold-welding, which, in turn, gives greater green strength to the compact. This increase in contacting surfaces also leads to more efficient sintering.

4.1.5 Surface Area

As interparticle bonds form due to compaction this provide the green strength. These solid interfaces are created by deformation at the initial point contacts between particles. Initial packing density aids the formation of interparticles bonds. When compaction pressure is sufficient shear forces will act to disrupt surface films. See Figure 26 for an example. Formation of flat contact regions is apparent. However, there is no evidence of cold working of contact regions being noticeable. Attractive forces are weak between the particles. Only after sintering that substantial strength is observed.

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Figure 26. Flat deformation face on the powder increased the surface area contact between powder during compaction[53].

Powder characteristic such as the particle size, handling of the powder and compaction will determine the initial porosity created.

Both alloying of the powder and powder characteristic are two factors that must have correct parameters and both are inter dependent on each other too. After which the samples are being compacted to a green body before proceeding to the next process known as sintering

4.2 Theory of Sintering

Sintering is a process of shaping powdered material parts is by de-nitrifying the powder material, metals, or ceramics, in a die and subsequently heating it to give the appropriate properties. Sintering is the bonding of particles in a mass of powder by molecular or atomic attraction in the solid state, by application of heat, causing strengthening of the powder mass and possibly resulting in densification and re-crystallisation by transport of materials[80]. The powder is styled to the required shape, normally at room temperature, with application of high-tonnage of compacting pressure. No binder or adhesive material is utilized in this operation. Then, the fragment specimen is heat-treated by the procedure known as sintering to induce optimal strength.

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Sintering is normally performed in a controlled-atmosphere furnace where the green part is heated to a temperature close to but not at melting. This is done so that elements may tie by solid state bonding, but not melt.

The theory of sintering can be presented as equations linking in some dimensional variables such as neck or pore radius or volume of compact, using time and temperature established during the process. Most sintering equations hold a number of parameters such as diffusion coefficient, surface tension, particles sizes, initial pore volume, etc. These can be split into 2 classes:

1. *Intrinsic* – these specify the intrinsic properties of the materials begin sintered, for example surface tension, diffusion coefficient, vapours pressure, viscosity, etc. These properties modify when the chemical composition, ambient atmosphere or temperature changes[80].
2. *Extrinsic* – these depend on the geometrical or topological details of a structure. They consist of parameters such, as average particle size, particle or pore or grain shape and size distribution, etc[80].

These two classes of parameters are in some way or other interdependent. Take for instance, fabrication of Al_2O_3 , manipulation of any chemistry within the system will prevent the formation of intermetallic, exaggerated grain growth, which in turn allows almost complete elimination of porosity.

4.2.1 Basic Thermodynamics of Sintering

The dynamic force for sintering is a reduction in the surface free energy of powdered compacts, by replacing solid-vapour interfaces (of surface energy Γ_{sv}) with solid-solid (Γ_{ss}) interfaces, where $\Gamma_{ss} < \Gamma_{sv}$. Thermodynamically, then, sintering is an irreversible process in which a free energy decrease is brought about by a decrease in surface area.

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At a typical specific surface S of ceramic powders $S = 1-10 \text{ m}^2/\text{g}$ and $\Gamma_{SV} = 1 - 2 \text{ J/m}^2$. The resulting excess of surface energy of $\Gamma_{SV} = 1-20 \text{ J/g}$ is small compared with the heat transfer of chemical reactions ($> 1 \text{ kJ/g}$) but still sufficient to drive the sintering processes. Some mechanisms can lead to a waste of sintering driving force without assisting densification. These are the grain coarsening mechanisms, which are driven by the same force as sintering.

The change of system energy dE due to sintering is therefore composed of the increase due to the creation of new grain boundary areas, $dA_{SS} > 0$, and due to the annihilation of vapour-solid interfaces, $dA_{SV} < 0$. The necessary global thermodynamic condition for the sintering to proceed is:

$$dE = \Gamma_{SS} dA_{SS} + \Gamma_{SV} dA_{SV} < 0 \quad \text{Equation 4-7}$$

The sintering process will stop when $dE = 0$, i.e. $\Gamma_{SS} dA_{SS} + \Gamma_{SV} dA_{SV} = 0$ or $\Gamma_{SS} / \Gamma_{SV} = -dA_{SV} / dA_{SS}$

The sintering progress can be represented by plotting the total free surface area A_{SV} , vs the total surface area of the grain boundaries A_{SS} . At the start of sintering, all surface area equals the free surface area, since no grain boundaries exist yet, $A_{SV} = A_{SV0}$ and $A_{SS} = 0$. As sintering proceeds, A_{SV} decreases and A_{SS} increases, in such a way that a monotonically decreasing curve is obtained with the slope $-dA_{SV} / dA_{SS}$. If at any point during sintering, the value of the slope reaches $\Gamma_{SS} / \Gamma_{SV}$, the sintering must stop due to the above equilibrium condition. The principal objective of sintering is the elimination of porosity, i.e. a minimum A_{SV} , possibly $A_{SV} = 0$ and A_{SS} large, meaning little grain growth. It is thus desirable that the sintering stop condition is reached when the slope dA_{SV} / dA_{SS} is close to zero, i.e. $\Gamma_{SS} \ll \Gamma_{SV}$. Through this type of thermodynamic considerations it is suggested that sintering can be encouraged through manipulation of the doping and/or the environment, so the surface energy is maximised.

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4.2.2 Sintering of multicomponent system

At present no quantitative predictions can be prepared about the densification rates on multicomponent systems. The reactions of the systems to sintering depends on the relative solubility of the species in one another, the comparative surface energies and relative diffusion rates. Material transport happens as a result of surface curvature and gradients in the concentrations of the atomic species. One major difficulty in understanding the exact means of operation of an additive is that so many alternative mechanisms for these processes exist. Thus, e.g. the additive can work as a second phase or as a solid solution.

As a second phase,

- providing a high diffusivity path way, e.g. liquid phase at the boundaries;
- providing a continuous low diffusivity pathway at the boundaries for diffusion across the boundary, which then acts to restrain grain boundary movement.

As a solid solution,

- enhancing diffusion coefficients for the controlling species in the lattice or parallel to the grain boundary by effecting the point defect concentrations in the boundary or lattice;
- slowing grain boundary movement by forming a segregated layer at the boundary which must then be pulled along by the boundary;
- altering the overall driving force for sintering by altering the ratio of grain boundary energy to free surface energy;
- slowing intrinsic grain boundary movement by reducing the diffusion coefficient for atom movement across the grain boundary, again by affecting the defect chemistry.

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4.2.3 Shrinkage and Swelling

Prior to sintering, the compact is brittle and its strength, known as *green strength*, is low. Bonding and fusion of the individual particles occur during sintering. The nature and strength of the bond between the particles depend on the mechanisms of diffusion, plastic flow, evaporation of volatile material in the compact, re-crystallisation, grain growth, and pore shrinkage. As the particles pull in the surrounding particles upon cooling of after sintering[81] shrinkage occurred.

An attempt to obtain a generalized shrinkage equation was made by Johnson [82]. He drew out his outcome from initial stage to intermediate stage sintering by analogy. Substituting the average neck radius by a fraction of the mean linear grain intercept D and the neck curvature H , he obtained the rate of volume shrinkage for simultaneous volume and grain boundary diffusion[80].

$$Dv/vdt=(H/D)K(D_vS_v + D_{GB}L_v) \quad \text{Equation 4-8}$$

where K is the constant, D_v the volume diffusion coefficient, D_{GB} the grain boundary diffusion coefficient, S_v the surface density of pore/solid interface, L_v the line density of the grain boundary/pore surface interactions.

4.2.4 Pores situated at grain boundaries between two grains or within one grain

According to Oel[83] or Tomandl and co-workers[84-87] the pore shrinkage is described approximately as

$$ds/dt=-c_p/s^2 \text{ with } c_p = 2(\sigma+\gamma)u_pV_m \quad \text{Equation 4-9}$$

s =pore radius, σ =surface energy of the pore, γ =grain boundary energy, u_p =mobility of the atoms filling the pore, V_m =mol. volume.

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Pores sitting on the grain boundaries occupy some part of the common area of grain boundary of two grains. Therefore, this part of the area is not effective for the grain boundary movement.

For pores within grains c_p very small. If these pores are neglected, then several other equations related to pore shrinkage can be found in the literature[88-94].

4.2.5 Pores located at triple junction

Pores may be surrounded by more than two grains either as a result of the voids from the initial state of sintering or if the length of the grain boundary where the pore is sitting becomes smaller than the pore diameter. These pores are treated like grains as polyhedrons (3d) or polygons (2d), however with different effective mobility constants ck . The motion vector is assumed to be always in the direction towards the pore centre.

4.2.6 Pores at special location

The pores within grain boundaries have a limited velocity of movement. If the motion of the grain boundary belonging to the pore moves faster, then the pore is released from the grain boundary and positioned within the grain. The pore mobility is assumed as $M_p = c_{sep}/s$ according to[92].

If a grain disappears, then several pores may come together. Therefore, pore coalescence is taken into account.

During sintering of Ti-6Al-4V expansion and contraction was examined using a dilatometer. The green compact was 6mm in diameter and length of 15mm and compact was heated in a vacuum of 10^{-3} Pa from room temperature to 1250°C at rate of 10°C min⁻¹. Figure 27 shows at about 700°C, the compact expanded slightly as temperature increased. From 750-800°C the compact shows abrupt expansion behaviour. This is attributed to the melting of aluminium. (This is attributed to the melting of aluminum [95, 96] explained this behaviour, as the formation of Kirkendall type voids by unilateral diffusion of aluminum into titanium and the induction of reaction heat by formation of

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Ti₃Al.). After 850°C, contraction owing to the densification started to occur. It is relatively close to the β transus temperature of titanium powders. Diffusivity of β -titanium is much higher than of α -titanium. It is speculated that mutual diffusion between titanium powder and master alloys activated through the range of temperatures in which titanium in β phase[97].

Figure 27 Expansion of Ti6Al4V green compact during sintering process[97].

Optical micrographs of microstructure of Ti-6Al-4V compact at 700, 900 and 1200°C are shown in Figure 28. The Compact at 700°C was about to show the expansion in Figure 27, little reaction was observed and titanium powder remained in as-compact shapes. At 900°C which is the β transus temperature of titanium powders, boundaries of titanium powder became dim. This implies that the diffusion of titanium started activating around this temperature. At 1200°C alloying and densification were over. Desired microstructures consisting of lenticular α with scattered pores were almost obtained.

Figure 28 Microstructure variation of Ti6Al4V compacts during sintering[95, 97]1]

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4.2.7 Sintered Material Density

The sintered density of a part depends on its green density and the sintering conditions in terms of temperature, time, and furnace atmosphere. As the value of these parameters increase, the sintering density increases. Also, the density increases with a less oxidizing type of furnace atmosphere.

One desire is to produce a part of high density without allowing much increase in density during sintering. The reasons are the following:

1. For structural parts, a higher sintered density is very desirable, as it leads to better mechanical properties.
2. For better dimensional accuracy, it is preferable to minimize the increase in density during sintering.

This can be achieved by using a powder of high compressibility. Such powder gives a high green density and allows in keeping the sintering temperature moderate. Another important benefit of such powder is that larger parts can be produced with a specific press tonnage.

4.2.8 Sintering atmosphere (vacuum or normal atmospheric pressure)

Apart from adjusting the composition and contamination contents, sintering atmosphere also affects the sintering mechanisms. Gas transport rates are high and major changes are possible in pore structure, grain shape, impurity content, and sintering kinetics through sintering atmosphere. For example, several materials processed in a halide atmosphere show minimal shrinkage but accelerated coarsening due to enhanced vapour transport. Other microstructural changes are apparent in grain faceting, grain growth, surface area and pore size. A rationale is essential to establish which atmospheres are most effective for impurity control, leading to the possible employment of highly active atmospheres. Pore mobility and pore size are affected by vapour transport, so there is an opportunity to

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independently influence the grain growth and pore transportable rates via temperature and atmosphere control.

Besides allowing composition adjustments, the sintering atmosphere affects the surface structure and in some instances gives a change in the vacancy population. This can be effective in metallic systems where oxidation and reduction cycles influence diffusion rates. Alternatively, vacuum sintering leads to preferential evaporation and loss of stoichiometry in surface regions.

4.2.9 Sintering Mechanisms

Sintering mechanisms are complex and depend on the composition of metal particles as well as the processing parameters.

Two stages of sintering are distinguished based on time and temperature: conventional and high temperature sintering. Some physical, chemical, and metallurgical phenomena are attributed to each stage. It is important to note that the phenomena attributed to the first stages (conventional) continue during high temperature sintering.

Early Stages:

1. **Homogenisation:** The as-cast, dendrite structure of the atomised particles is removed and microsegregation within the particles is eliminated. Diffusion between powder particles begins to occur.
2. **Alloying:** As the diffusion process continues, mixed additives begin to form alloyed structures with the base ferrous particles. If one element has a lower melting point than the other, it may melt, and its particles then surround the particles that have not melted by surface tension (*liquid-phase sintering*). Stronger and denser parts can be produced this way such as when cobalt melts in tungsten-carbide parts. For species such as carbon, diffusion takes place early in the sintering process. For elements such as nickel or molybdenum, diffusion is much slower and takes longer times and higher temperatures to achieve a reasonable level of homogeneity.

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3. **Removal of gases/oxides:** Chemical reactions between the sintering atmosphere or admixed additives such as graphite and the surface oxides on the metal particles also begins early in the sintering cycle. This breakdown of oxides and removal of absorbed gases cleanses the metal particle surfaces and promotes the diffusion process.
4. **Particle bonding:** The formation of solid bridges or necks between individual or clusters of powder particles is the critical result of the early stages of sintering. These particle bonds give the powder mass integrity and mechanical strength.

Advanced Stages:

1. **Densification:** As the sintering process continues at higher temperatures, the inherent porosity in the powder mass is reduced as pores are eliminated by bulk diffusion to grain boundaries. This reduction in the amount of porosity results in an increase in the density of the powder compact.
2. **Porosity shape:** The remaining pores in the P/M structures lose their angular, irregular nature and become smooth, tending toward perfect spheres, as the sintering temperature increases.
3. **Grain growth:** The individual powder particles lose their identity completely as grain boundaries move across prior particle boundaries. Larger grains replace the original fine particle structure.
4. **Liquid phase:** Depending on the chemical constituents in the powder mass and the sintering temperature, a transient or permanent liquid phase may be formed. This liquid phase will accelerate particle rearrangement and diffusion, thereby aiding densification and pore elimination. For some additives, such as copper and phosphorus, liquid phase sintering will occur at conventional temperatures, while for silicon iron and tool steels high temperature sintering is required.

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On the macro level, as the degree of sintering improves, as indicated by a higher sintering temperature, the properties of the material such as strength, density, ductility, and thermal and electrical conductivities increase.

4.3 Solid State sintering

4.3.1 Mechanisms of Mass Transport and Neck Growth in Solid State Sintering

Transport mechanisms determine how mass flows in response to the driving force provided by the driving force of sintering. Figure 29 demonstrate a two-sphere model with two classes of mechanisms, surface transport and bulk transport.

For each model composed of several actual atomistic mechanisms contributing to mass flow. Surface transport processes produce neck growth without a change in particles spacing (no shrinkage or densification) due to mass flow originating and terminating at the particle surface. Surface diffusion and evaporation-condensation are the two most important contributors during surface transport-controlled sintering.

Surface diffusion dominates the low-temperature sintering of many metal. Evaporation-condensation is not as widespread, but dominates the sintering of low-stability material such as lead and lead-based compound (see Figure 29)

Both surface and bulk transport processes promote neck growth; the main difference is the shrinkage during sintering (see Figure 29). For densification to occur, the mass must originate from the particles interior with deposition at the neck. Bulk transport mechanisms include volume diffusion, grain boundary diffusion, plastic flow and viscous flow. Plastic flow is usually important only during the heating period, especially for compacted powders, where initial dislocation density is high. Surface tension stresses are generally insufficient to generate new dislocations. Plastic flow's role is decreased as the dislocations are annealed out of crystalline powder at high temperatures.

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In contrast, amorphous materials, such as glasses and polymers, sinter by viscous flow, where the particles coalesce at rates that depend on the particle size and material viscosity. A form of viscosity is also possible for metals with liquid phases on the grain boundaries. Grain boundary diffusion is fairly important to densification for most crystalline materials and appears to dominate the densification of many common systems. However, bulk transport processes are most active at higher temperature.

Figure 29 Sintering Mechanisms as applied to the two-sphere sintering model.

4.3.2 Mass transport from surfaces: evaporation-condensation

The mass transport can proceed through a gas phase, driven by a differential in vapour pressure. Evaporation-condensation takes place because the vapour pressure p_1 on a curved surface of radius r_1 is different from that on a flat surface (p_0 , $r_0 = \infty$) or any other surface at r_2 . This is expressed by the Kelvin equation:

$$\ln (p_1/p_2) = (\Omega \Gamma_{sv} / RT) (1/r_1 + 1/r_2) \quad \text{Equation 4-10}$$

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where Ω = the molar volume of the species. For the simple case of $r_2 = r_0 = \infty$ and $p_2 = p_0$ (that is, for a flat surface), the above equation simplifies to:

$$\ln(p_1/p_2) \approx (p_1 - p_0)/p_0 = \Delta p/p_0 \quad \text{so} \quad \Delta p/p_0 = (\Omega \Gamma_{sv})/(R T r_1) \quad \text{Equation 4-11}$$

Accordingly, convex surfaces show overpressure ($r_1 > 0$, $\Delta p > 0$), whereas concave surfaces show underpressure ($r_1 < 0$, $\Delta p < 0$). The pressure gradient results in faster evaporation from convex surfaces (i.e. from grains, especially small grains), transport under the pressure gradient, and condensation within concave surfaces (i.e. within necks). Quantitatively, the effect is not large. For example $\Delta p/p_0 = 1.02$ for SiO_2 of $r_1 = 10^{-7}$ m (0.1 μm) at 1700°C .

The most important case of evaporation-condensation mass transport is from the surface of convex (spherical) particles ($r > 0$) to the surface of concave necks ($r_n < 0$) where $|r_n| \ll |r|$ at the contact region. No shrinkage occurs in this process and y^3 is a linear function of time (See Figure 29):

$$y^3 = \alpha_2 t \quad \text{and} \quad h/r = \Delta L/L_0 = 0 \quad \text{Equation 4-12}$$

This type of transport dominates at the relatively high vapour pressures of 10^{-4} atmospheres, found for halides (e.g. NaCl at 700°C). The log-log plot of the neck size versus time has a slope close to $1/3$. The evaporation - condensation process is suspected to stop the sinterability of some non-oxide ceramics (such as SiC , B_4C) at very high temperatures $> 2100^\circ\text{C}$.

This type of mass transport is desirable and applicable to the manufacturing biomaterial implant that this project is aiming in production a porous implant.

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4.3.3 Models for mass transport from surfaces: surface or volume diffusion from surface

Similar to evaporation/condensation, no shrinkage results from the other two mechanisms of mass transport from particle surfaces to necks through the two possible diffusion paths.

1. volume diffusion from particle surfaces to necks:

$$y^4 = \alpha_3 t \text{ and } h/r = \Delta L/L = 0 \quad \text{Equation 4-13}$$

surface diffusion, along particle surfaces to necks:

$$y^7 = \alpha_4 t \text{ and } h/r = \Delta L/L = 0 \quad \text{Equation 4-14}$$

As the volume diffusion is governed by higher sintering temperature, it is not much of a concern, as high temperature sintering will not be actually taking place. As temperature will be high but formation of a small fraction of liquid, which allow only the surface diffusion to take place and cooling rate will be fast.

4.3.4 The model for mass transport from within the particle volume or from the grain boundary

For mass transfer originating in the particle volume or at the grain boundary, the particle centres approach ($h > 0$) and shrinkage takes place.

1. for volume diffusion from grain boundary:

$$y^5 = \alpha_5 t \text{ and thus } (h/r)^{2.5} = (\Delta L/L)^{2.5} = \beta_5 t \quad \text{Equation 4-15}$$

2. for grain boundary diffusion from grain boundary:

$$y^6 = \alpha_6 t \text{ and thus } (h/r)^3 = (\Delta L/L)^3 = \beta_6 t \quad \text{Equation 4-16}$$

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Knowing the relationships of the type $y^n = \alpha t$ for different mass transport mechanisms, model experiments can be performed on presumably ideal compacts of spheres, according to the following plan:

- measure compact shrinkage $s = \Delta L/L$ versus time t : s_1 at t_1 , s_2 at t_2 , etc.
- plot $\log s$ versus $\log t$, determine slope n , and find equation $s^n = \beta t$
- compare the calculated n with the values characteristic for various mass transfer processes and determine the sintering mechanism. If the sintering mechanism is known, the optimum sintering procedures can be proposed.
- knowing the average initial particle radius r , calculate the neck radius y at different times (See Figure 29)

As $h = y^2/4r$, then $y(t) = 2\sqrt{r}(\beta t)^{1/2n}$. Similar calculations can be performed if the neck radius $y(t)$ is measured directly.

For diffusion-controlled mechanisms, α_i and β_i are proportional to the diffusion coefficient $D = D_0 \exp(-H/RT)$, where H is the activation energy for diffusion. For viscous flow sintering α_i and β_i are inversely proportional to the viscosity coefficient η , where $\eta = \eta_0 \exp(Q/RT)$ and Q is the activation energy for viscous flow. NOTE, that temperature has an exponential effect on the two above modes of sintering.

Conversely, for evaporation-condensation, α is proportional to vapour pressure and therefore is linear with temperature ($pV=RT$). It is therefore frequently found, that the detrimental evaporation-condensation mechanisms are predominant at lower temperatures, whereas viscous flow and/or diffusional sintering take over at higher temperatures. If it is desired to avoid substantial particles growth through evaporation-condensation before densification (i.e. in most cases of sintering), fast heating rate is recommended.

Sintering kinetics is accelerated for:

- fine grained materials;
- elevated temperatures

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- high surface energy

The powder composition and sintering atmosphere intervene in the densification through modification of the diffusion coefficient D . However, increasing the temperature far beyond $T = 0.5T_m$ does not guarantee an increased sintering rate and full densification. This is due to the coarsening of grains (as explained above, through evaporation/condensation and surface diffusion) that can effectively stop densification (compaction through volume diffusion and grain boundary diffusion).

Therefore for this project, the desired mass transport mechanism to create a porous biomaterial should have the following transport taking place:

- Evaporation-condensation
- Surface diffusion
- Grain Boundary diffusion(in small amount)

In a study made by Namjoshi and Thadhani[98] of Ti-Si powder mixtures at ~ 5 GPa, results in lowering of the obvious activation energy of about 106 kJ/mol which is about two-thirds of that accounted for Si diffusion into Ti. Consequently, the reaction behaviours of dynamically densified Ti-Si powder mixtures at 800–900°C (See Figure 30), is subjected by a solid-state diffusion reaction forming up to 70% Ti_5Si_3 reaction product in about 5 hours. With a further raise in temperature up to 1000°C, about 40–50% reaction occurs in the solid state, and the remaining reaction is taken over by a combustion-type dissolution-precipitation process showing Johnson-Mehl Avrami(JMA)(see Equation 4-17)[99] kinetics. Complete reaction, forming Ti_5Si_3 product is thus observed in less than 5 hour hold times at 1000°C. Shock-densification is thus, observed to lower the apparent activation energy for solid-state diffusion reactions in Ti-Si powder mixtures, thereby allowing control over the degree of reaction occurring in the solid-state or via the combustion mechanism to tailor the reaction synthesis process and reaction product microstructure.

$$x(t)=1-\exp(-kt^n), \quad \text{Equation 4-17}$$

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Figure 30 (a) A plot of ΔT vs temperature for the Ti-Si PBB compact for different heating rates. (b) A plot of ΔT vs time for the Ti-Si PBB compact for different heating rates[98]. Δt is the change in temperature.

4.4 Liquid phase sintering

Activated sintering allows for either a lower sintering temperature, a shorter sintering time, or improvement in properties from a chemical addition to the powder. One of the most dramatic examples of activated sintering occurs when tungsten or molybdenum is treated with certain transition metals[100, 101]. German [102] proposed an ideal phase diagram for activated sintering systems involving factors like solubility, segregation and diffusion, as described below:

- **Solubility.** The additive must have solubility in the base metal in order to exhibit a favourable effect on diffusion.

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- *Segregation.* During sintering, the additive must remain segregated at the interparticle interfaces to remain effective during the entire sintering cycle.
- *Diffusion.* $D_E > D_B$, where D_E is the diffusivity of the base metal B in the additive layer, and D_B is the self-diffusivity of the base metal B.

In two-phase systems involving mixed powders, liquid formation is possible because of different melting ranges for the components. In such a system, the liquid may provide for rapid transport and therefore sintering if certain criteria are met. These criteria are similar to those for activated sintering.

A number of workers[80] critically analyzed activated sintering, which according to Lenel[103] is a misnomer and must be viewed in the framework of the generalized sintering theory. Kuczynski[104] agreed in principle with Lenel[103]; however he felt it difficult to abandon the term as its usage has come to stay in technology. The work of Samsonov et al.[105] elegantly illustrated the role of electronic structure in 'activated sintering' processes, where the material composition must be changed.

Figure 31 is a schematic drawing showing three contacting particles during supersolidus liquid phase sintering (SLPS). Liquid forms at the interparticle contacts and the grain boundaries within the particles. The liquid accumulated at interparticle contacts exerts a capillary force on the adjoining particles, while the liquid at the grain boundaries is responsible for loss of particle rigidity. Initial densification occurs by localized deformation in a small region near the neck (where capillary force provides a high compressive stress) that results in neck growth and contact flattening [106]. However, this becomes possible only when the grain boundaries are sufficiently weakened by liquid films[101].

$$\sigma_{\text{cap}} = 5.2 \gamma_{\text{LV}} \cos(\theta) / D(\Delta L/L_0) \quad \text{Equation 4-18}$$

where D is the particle diameter, γ_{LV} is the liquid–vapor surface energy, θ is the wetting angle ($\approx 0^\circ$ for wetting liquid), and $\Delta L/L_0$ is the sintering shrinkage (compact length change divided by initial length). Typical initial values for σ_{cap} are of the order of a few MPa (for a γ_{LV} of 2 J/m² and particle size of 100 μm , the capillary stress goes from 10 to 1 MPa as the linear shrinkage goes from 0.01 to 0.1).

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Figure 31 A porous compact during early stages of densification is shown. The inset shows three particles where liquid forms at the particle contacts, at the grain boundaries, and within the solid grains. The capillary force due to the liquid at the particle contacts drives densification by exerting a net hydrostatic stress on the structure[101].

To conceptualize shape loss due to gravity, consider the compact shown in Figure 31. The gravitational force provides a net deviatoric component acting in the axial direction. The pressure developed from the top head of the component mass is responsible for shape loss. The stress at any point depends on the cumulative mass above it, and is given by $h\rho g$ (for a compact of uniform cross-section throughout), where h is the height from the top, g is acceleration due to gravity, and ρ is the density. The stress at the bottom of a sample with a height of 0.01 m and density 10 g/cm³ is about 1 kPa. This is much lower in magnitude than the capillary stress responsible for densification.

In SLPS the particles are semisolid, and can deform individually in response to the gravitational force. Compact shape loss occurs due to the deformation of the entire particle, or alternatively, the entire compact after densification. Since the capillary stress is much larger than the gravitational force, during densification, the effect of gravity is negligible. After densification, the compact consists of solid grains with liquid at the grain boundaries and negligible porosity. Once the voids are filled with liquid (saturated), the capillary force approaches zero, while gravitational force acts downward (such that the resulting force field has a shear component). The compact slumps when the solid-liquid structure is weak when compared to gravity. The result is compression in the axial direction and expansion in the radial direction. A non-uniform shape change results since the magnitude of the gravitational stress increases with the height from the top. Thus, the

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radial expansion is the least at the top and largest near the bottom (disregarding substrate friction).

4.5 Transient Liquid Phase Sintering

Liquid reduces the interparticle friction, thereby aiding rapid rearrangement of the solid particles, and liquid dissolution of sharp particles edges and corners allows more efficient packing (See Figure 32). The transient liquid phase sintering process, termed ISM (in situ microfusion) process, has recently been developed[107]. It is an exothermic reaction between two elemental powders is used to provide a small volume of liquid. Transient liquid-phase sintering (TLPS) offers a number of processing advantages over solid-state sintering including[108]:

1. rapid densification,
2. lower sintering temperatures,
3. use of less expensive elemental powders versus alloyed powders,
4. reduced microstructural coarsening, and
5. improvement in the mechanical properties

Parameters, which influence the volume of liquid, are the compaction pressure, powder size and identification of the intermetallic phase[108] and enhanced mass transport and densification[109]. The control of the liquid volume and the relationship between the densification and the liquid volume has been considered. Transient liquid phase sintering process utilised the exothermic reaction and the consequential phase from the exothermic reaction is an intermetallic compound and the melting temperature is the eutectic temperature of alloy system. The liquid phase is necessary for densification or full densification and requires an optimum liquid volume (8-12 volume %) that is dependent on the compaction pressure (242-362 MPa)[110], enhanced mass transport and densification. Densification occurs only in the rearrangement stage and the lifetime of the liquid is very short, for only a few minutes. Therefore the liquid volume, the distribution of the liquid and the compaction pressure are much more important in the transient liquid phase sintering process than in the conventional liquid phase sintering process. The furnace temperature, amount of the powder in the reaction process, the reaction

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temperature and the distribution of liquid due to both the compaction pressure and the powder size mainly control the liquid volume[107, 111].

The optimum liquid volume fraction in the process is 8-12 volume % depending on the compaction pressure[110]. But Kingery gave a 35-volume % and it has been a criterion value for the rearrangement process in conventional liquid phase sintering[112]. There is no optimum liquid volume found for any particular transient liquid phase sintering. The reason might be the difficulties in the estimation of the liquid volume during sintering and/or the establishment of a suitable system for the particular sintering process[107].

Figure 32 The stages of TLPS in a powder mixture consisting of low melting point additive powder A and high melting point base powder B[113].

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4.5.1 Liquid - Solid Interactions during Liquid Sintering

During sintering, the interaction of a non-reactive liquid with an insoluble solid could result in some or all of the following mechanism taking place:

- sintering is controlled by properties of the liquid phase, with the solid behaving as an inert filler.
- the densification mechanism is that the liquid simply fills the interstitial space between solid particles.
- usually a relatively large amount of liquid (20-40 vol. %) is necessary to accomplish this.
- the densification mechanism is such that solid particles only rearrange themselves due to the viscous drag of the liquid and capillary pressure p within pores of radius r_p :

$$p = 2\Gamma_{lv}/r_p \quad \text{Equation 4-19}$$

where Γ_{lv} is the surface tension of the liquid/vapour interface.

- for typical value of surface tension $\Gamma_{lv} = 1 \text{ N/m} = 1 \text{ J/m}^2$ and $r_p = 0.1 \text{ }\mu\text{m}$, $p = 2.6 \text{ MPa}$ (26 atm), a pressure sufficiently high to sustain particle movement, leading to rearrangement and densification.
- this system is less important in ceramics, since the high processing temperatures usually triggers substantial reactivity between the solid and liquid.

The solid is well wetted and dissolves in the liquid:

- usually < 20 vol% liquid is sufficient for active densification in this system.

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- on top of the above mechanisms, viscous drag and capillary pressure driven rearrangement, the solids dissolve and precipitate in the pores.

The dissolution process is especially fast in areas of increased activity, such as:

- **high curvature surfaces**, which results in increased solubility of small particles.
- The solubility S of a particle of $r < \infty$ is increased over that of a flat ($r = \infty$) surface's solubility S_0 according to the Gibbs-Thomson equation:

$$\ln (S/S_0) = 2\Gamma_{sl} M / (R T r) \quad \text{Equation 4-20}$$

where M = the molar volume of the dissolving species. This is not a large effect. At $\Gamma_{sl} = 0.4 \text{ N/m}$ (this value was taken for Fe in Cu at 1200°C) and $r = 1 \text{ }\mu\text{m}$, the solubility of Fe particles in liquid Cu increases over that of a flat surface by only 0.5%, or $S/S_0 = 1.005$.

- **particle contact points** under the pressure of capillary force, resulting from the negative curvature ($=1/r_n$) of the liquid film in neck area, causes increased activity a/a_0 in the solute

$$\ln a/a_0 = 2k\Gamma_{lv} M / (R T r_n) \quad \text{Equation 4-21}$$

where k = constant.

Typically, $r_n < 0.1r$, where r = particle radius, and capillary pressure is of the order of 100 atm at $r = 1\text{ }\mu\text{m}$ and $\Gamma_{lv} = 1\text{ J/m}^2$. This is a large effect. For Fe in Cu at 1200°C and $r_n = 0.1 \text{ }\mu\text{m}$, the activity of dissolved Fe in equilibrium with a surface under pressure increases by 14% ($a/a_0 = 1.14$) over that of dissolved Fe dissolved in equilibrium with a pressure free surface.

4.5.2 The effect of the surface energy balance on liquid - solid interactions

During liquid sintering, the total surface free energy of the system is continuously minimised. Simultaneously, the balance of surface energy is of primary importance in

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the wetting of the solid by the liquid. Generally, surface tension at the liquid/vapour interface decreases with temperature. That is,

$$\Gamma_{lv} = \Gamma_o (1 - T/T_c)^n \quad ; \quad \Gamma_{lv} = 0 \text{ at } T = T_c \quad \text{Equation 4-22}$$

where $n \cong 1.2$, T_c is the critical temperature, and Γ_o is a material parameter ($= \Gamma_{lv}$ at $T = 0K$).

Surface energy determines the magnitude of the vapour pressure excess Δp on a curved surface, compared to the equilibrium pressure on a flat surface:

$$\Delta p = 2\Gamma_{lv}/r \quad \text{Equation 4-23}$$

Surface tension determines the magnitude of the adhesion pressure between grains separated by a liquid film of thickness d :

$$\Delta p = 2\Gamma_{lv} \cos\theta/d \quad \text{Equation 4-24}$$

Where θ is the contact or wetting angle. If $\theta < 90$ (a wetting liquid), $\Delta p > 0 \rightarrow$ attraction of particles. If $\theta > 90$ (a non-wetting liquid), $\Delta p < 0 \rightarrow$ repulsion of particles.

Because of particle repulsion at $\theta > 90^\circ$, a powdered solid can not be densified with the assistance of a non-wetting liquid. At best, the effect of such a process is partial solid state sintering, with the liquid exuded from the solid.

4.5.3 Shape retention in sintered parts

From technological viewpoint, shape retention of sintered parts is very essential. The problem is more severe in liquid phase sintered parts. German [101] has carried out numerous investigations to correlate distortion with microstructural parameters. The rigidity of microstructure was described in terms of the total average bond force per

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grains (See Figure 33). It depends on the extent of solid–solid contact and the grain adhesion by the grain boundary liquid. German[79] showed that the resistance to densification and distortion goes down with an increase in the liquid content if there is a decrease in the connectivity and an increase in liquid film thickness. The grain coarsening and the resulting liquid film coarsening cause a drop in the microstructural rigidity. This attempt, no doubt, rationalises the preliminary microstructural attributes, but it is still far away from the real engineering solution.

Figure 33 A compact after near complete densification is shown. The inset shows the structure consisting of solid grains with liquid at the grain boundaries (and some liquid within the grains). The porosity and the capillary force are negligible at this stage. However, the component mass provides a force in the axial direction that increases with height from the top, possibly leading to shape distortion[77, 101, 114].

Sintering will be the final stage in forming of the implant to be used for *in-vivo* and *in-vitro* testing on animals. It is an important process with the control of the temperature, time, and rate of heating for formation of the liquid required in binding the powder together. Furthermore, it controls the formation of the pores and strength of the implant.

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5 Experimental Methods and Equipments

On initially receiving of the powders, the Certificate of Analysis (Table 9) was scrutinized to check on the as-received powder purity, average particle size and lot number for each material.

Table 9 As-received powders particle sizes and purity (CERAc Inc., USA)

Chemical Name	Lot Number	Purity	Particle Sizes
Zirconium Metal (Zr)	X0027391	94-98%	2-5µm
Titanium Metal (Ti)	X25822	99.9%(Na<10ppm)	74µm
Silicon Metal (Si)	303179-1WT	99.96%	44-74µm
Aluminium Metal (Al)	603048-1	99.5%	44-74µm
Vanadium Metal (V)	X13213	99.7%	44µm
Nickel Metal (Ni)	X0026878	99.9%	5µm
Titanium Hydride (TiH ₂)	X0024868	99.9%	43µm

A reference material wouldl be created known as Ti6Al4V. This material would be made with the as-received powder, pressed and sintered to from an α+β alloy. Forming a guide for the sintering and characterization of the Ti-Si-Zr material

Mechanical alloying of Nickel-titanium was carried out, since up until today most research was based on using elementary powders to create the porous NiTi for permanent skeletal replacement implant[115]. For this research, some mechanical alloyed powder of NiTi was added to the pure elemental powders. It will assist in the formation Ni-Ti at a lower temperature during the reaction process. This is to establish some guidelines for the milling parameters for the Ti-Si powder at eutectic composition.

Experiments to determine the manufacturing process of Ti-Si-Zr (Traditional Sintering) are split into two processes performed concurrently. The first will be creating of the Ti-Si, which would be mechanically alloyed to act as a glue. The second process will be the blending of the alloyed Ti-Si with the elementary Ti-Zr powder to form the Ti-Si-Zr material. After a thorough blending for 8hours the Ti-Si-Zr mix will be sintered to form the material. Adding of Titanium hydride a foaming reagent to assist in the pore formation during the sintering process.

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5.1 Equipments Used for the Experiment

5.1.1 Mechanical Alloy Equipments

Accurately weighed powders were then added to the vial-ball assemble. To prevent the excessive welding in the vial, 1 wt.% of alcohol was also added to the system as the processing control agent. The vial was sealed with adhesive tape inside the glove box under flowing argon gas. Mechanical alloying (MA) of the mixture was conducted in a Retsch mill (Model PM-400). Milling was done at room temperature in a stainless steel vial with stainless steel balls under an argon atmosphere. The milling speed and the ball-to-powder charge ratio were 200 rpm and 15 respectively. The milling was interrupted at regular intervals to collect samples for microstructure and phase analyses.

5.1.2 Glove Box

The powders are process in Mbraun glove box under continuous flowing of inert argon environment. The glove box is kept a level of 1 part per million (ppm) of water and oxygen to ensure that contamination of the powders was kept to the lowest level.

5.1.3 The Furnace

Sintering of the material was carried out in an Oxy-Gon furnace in a vacuum environment (up to 10^{-4} torr of atmosphere) at a heating rate of 5 deg/min and cooling rate of 5 deg/min. The sample is furnace cooled. Sintering temperature is 750~1050°C and with a holding time of 3 hours.

5.1.4 Hydraulic Press and Compacting Die

Compactions of the elemental powders were performed with a die of diameter 12mm and height of 10mm(weight of the powder is 3grams). The material used for the die was made of tool steel. Weight was recorded with Precisa 180A and the density calculated. The hydraulic press used is 0.71MPa.

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5.1.5 Characterization Equipments

The assistance of X-ray diffraction (XRD) analysis was performed on a Philips X'pert X-ray diffractometer with $\text{CuK}\alpha$ radiation at 40 kV and 30 mA. A JEOL JSM-5600LV scanning electron microscopy (SEM) was used to observe the powder morphology operated at 20 kV equipped with an energy dispersive spectroscopy (EDX) unit. Transmission electron microscopy (TEM) was performed on a JEOL 2000 microscope operated at 200 kV.

Differential Thermal Analysis (DTA) was used to determine the formation of liquid phase of the MA Ti-Si. This is to assist in the sintering process. With a quick wetting occurring, which allowed a grain boundaries and surface diffusion to take place for the Ti-Si melts. The Ti-Si will hold the pure Ti and Zr in place and the melted and diffused Ti-Si into the Ti and Zr will create the pores required (by theory by German[53]).

5.2 Powder Material Composition (Mechanical Alloying)

The powders were processed and mixed in the glove box in constant flow of inert gas argon. This ensures the purity of the powder mixture and prevent oxidation or contamination of the powders to the minimum.

5.2.1 Ti6Al4V

Elementary powders of Ti (74 μm , 99.9% purity, CERAc Inc., USA), Al (44-74 μm , purity 99.5, CERAc Inc., USA) and vanadium (44 μm , purity 99.7%, CERAc Inc., USA) were used. They were mixed in the ratio of 90% of the titanium, 6% of the aluminium and 4% of the vanadium

5.2.2 NiTi

Elemental powders of titanium (74 μm , 99.9% purity, CERAc Inc., USA) and nickel (5 μm , 99.9% purity, CERAc Inc., USA) powders were mixed to give the desired equiatomic composition in a glove box under a purified argon atmosphere.

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Figure 34 NiTi Flowchart of the Mechanically Alloyed powder

5.2.3 Ti-Si

Mechanical alloying of Ti-Si powder at a composition mix of eutectic point with the elemental Ti (74 μ m, 99.9% purity, CERAc Inc., USA) and Si (44-74 μ m, 99.96% purity, CERAc Inc., USA) powders were used as the feedstocks. The morphologies of Ti and Si powders are shown in Figure 38. The Ti:Si ratio was chosen based on the eutectic composition at 1330°C, which contained 13.5 at.% Si, i.e., Ti_{86.5}Si_{13.5}. Accurately weighed Ti and Si powders were added to vial-ball assembly in a glove box for mechanical alloying.

Calculation of Mixing ratio of Ti-Si(alloyed powders) to Ti-Zr(unalloyed powders) mix with addition of TiH₂(foaming agent)

Before mixing the powders, the amount of weight of each powder must be calculated so that the appropriate concentration will be used. These calculations are shown below:

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Symbols:

X_{Si} : weight percentage of Si in Ti-Zr-Si system

C_{Si} : weight percentage of Si at eutectic point, which is 8.44 wt. %

m_{MA} : mass of MA powders

$m_{Ti}^{'}$: mass of Ti raw powder

$m_{Ti}^{''}$: mass of Ti from MA powder

m_{Zr} : mass of Zr powder

C_{Zr} : weight percentage of Zr at 7 at. % Zr in Ti-Zr system, which is 14.6 wt. %

assume:

$$m_{MA} + m_{Ti}^{' } + m_{Zr} = 100 \text{ g} \quad \text{Equation 5-1}$$

$$X_{Si} = (C_{Si} \times m_{MA}) / (m_{MA} + m_{Ti}^{' }) \quad \text{Equation 5-2}$$

From (Equation 5-1) & (Equation 5-1),

$$X_{Si} = (8.44 \text{ wt. \%} \times m_{MA}) / (100 - m_{Zr}) \quad \text{Equation 5-3}$$

$$m_{Ti}^{''} = ((\text{Equation 5-1}) - C_{Si}) \times m_{MA} = 91.56\% \times m_{MA} \quad \text{Equation 5-4}$$

$$\text{From (Equation 5-1): } m_{Ti}^{' } + m_{Zr} = 100 - m_{MA} \quad \text{Equation 5-5}$$

As weight percentage of Zr is 14.6 wt. %, then

$$m_{Zr} = C_{Zr} \times (m_{Ti}^{' } + m_{Zr} + m_{Ti}^{''}) \quad \text{Equation 5-6}$$

From (Equation 5-1), (Equation 5-4) & (Equation 5-6):

$$\begin{aligned} m_{Zr} &= 14.6 \text{ wt. \%} \times [(100 - m_{MA}) + 91.56\% \times m_{MA}] = 14.6\% \times [100 - 8.44\% \times m_{MA}] \\ &= 14.6 - 1.23\% \times m_{MA} \end{aligned} \quad \text{Equation 5-7}$$

From (Equation 5-3) & (Equation 5-7):

$$\begin{aligned} X_{Si} &= (8.44 \text{ wt. \%} \times m_{MA}) / [100 - (14.6 - 1.23\% \times m_{MA})] \\ &= 8.44\% m_{MA} / [85.4 + 1.23 m_{MA}] \end{aligned} \quad \text{Equation 5-8}$$

After these calculations were done, the mix was prepared in the glove box under an argon environment. This is to ensure that the contamination level was minimized to the least possible level and positively ensure the right amount of mixture was prepared.

The Ti-Si alloyed powder was mechanical alloyed, with the simply reason that it acted as an important gluing agent to lock the titanium powder and zirconium powder together

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with a temperature driven sintering process. MA Ti-Si powders possessed lower melting point, along with fine grain size and the relative large amount of energy gained during the mechanical alloying process. This MA powder will melt at a low temperature to form a relative small amount of liquid to surround the titanium and zirconium powder and lock them in place thus omitting the brittle phase that could be formed.

The TiSi alloyed powder is mixed in a proportion of 91.74% of titanium, 8.26% of silicon and 7% of zirconium. For 87gram of powder, the necessary calculation was done to obtain the composition. Therefore the composition is 91.74 wt.% of titanium and 8.26 wt.% of silicon. The mixture was then put into a vial, for milling.

To increase the formation of pores within the system, titanium hydride (TiH_2) as a foaming agent was introduced. With the new addition of this TiH_2 powders, the amount of the titanium reduced in the system, this was to balance out the amount of Ti powders added to the system. Two variation of the TiH_2 mixed with 40% and 80% were used.

Mechanical alloying (MA) of the mixture was conducted in a Retsch mill (Model PM-400). Milling was done at room temperature (25°C) in a stainless steel vial with stainless steel balls under a purified argon atmosphere. To prevent excessive welding in the vial, 1 wt.% of alcohol was added to the system as the processing control agent. The milling speed and the ball to powder charge ratio were 200 rpm and 15, respectively. The milling was interrupted at regular intervals to collect samples for structure analysis.

X-ray diffraction (XRD) analysis was performed with $\text{CuK}\alpha$ radiation at 40 kV and 30 mA. A diffraction angle between 20 and 120° was employed. The solid solubility levels of Si in Ti achieved after mechanical alloying were evaluated by calculating the lattice parameters of Ti from XRD patterns. The lattice parameters a and c of Ti(Si) solid solution were calculated from the high-angle diffraction peak position. The volume of the unit cell for hexagonal Ti was obtained by the following equation:

$$V = \frac{\sqrt{3}a^2c}{2} \quad \text{Equation 5-9}$$

in which V is the unit cell volume, a and c are the lattice parameters.

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5.3 Compaction Ti6Al4V (MA powder and as-received powder) and Ti-Si (MA powder)

After milling, the powder will be compacted with the help of the hydraulic press and each powder will be pressed using a die made of tool steel. Each powder was pressed with 1 and 2ton pressure.

The density of powder of Ti6Al4V was calculated by the following formula:

$$\text{Density} = \text{mass} / \text{volume} \quad \text{Equation 5-10}$$

where mass is grammes, measured the weight of sample after cold pressing
volume is found by the following formula:

$$\text{Volume} = \pi r^2 / h \quad \text{Equation 5-11}$$

where $\pi = 3.1425$, r = radius of circle and h = height of the sample in mm

After the density of the pressed powder was determined, dividing the calculated density with the theoretical density multiply by 100%, the relative percentage was found. Therefore, the relative density percentage was obtained. After sintering the samples, measurement was taken again and calculation as similar as before. Taking the difference of the densities before and after sintering the density change in percentage terms can be obtained.

5.4 Results and discussion of the Mechanical Alloyed powders

This section shows the outcome of the powders. When the were powders subjected to mechanical alloying with different number of alloying hours.

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5.4.1 Effect and Result of Mechanical Alloying Ni-Ti

Figure 35 shows the surface morphology of Ni-Ti powders after mechanical alloying at various milling times, which illustrate the change of particle size and morphology. Before ball milling, the nickel powders had a mean particle size of 5 μm and are uniformly distributed in the titanium powders. The titanium powders are angular in shape and have a particle size of $\sim 50 \mu\text{m}$. As is known, the ball milling process involves the repeated welding, fracturing and rewelding of powder particles. After ball milling, the particles become considerably smaller in size and granular in shape (Figure 35b-d). Milling at 90hr (Figure 35e) shows the specific increase in powder size due to the agglomeration of particles into larger aggregates. With further milling, the powders become more homogeneous while keeping the granular morphology (Figure 35f).

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(a)0hr

(b)10hr

(c)30hr

(d)60hr

(e)90hr

(f)120hr

Figure 35 SEM morphology of mechanically alloyed Ni-Ti powders

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EDX analysis of the powders shows that the Fe and Cr impurities increase with the milling time due to the wear debris of the steel milling media during the milling process (Figure 36). Small amounts of Fe (1.59 at.%) and Cr (0.81 at.%) are obtained after 75 hr milling. With the further increase in the milling time, the level of impurities increases significantly and the impurity contents of Fe and Cr reach 20.75 at.% and 4.7 at.%, respectively after 120 hr milling.

Figure 37 shows the XRD patterns of Ni-Ti powders after mechanical alloying for various periods of time. The Ni-Ti powders obtained by mechanical alloying are obviously nanocrystallized solid solution as evidenced by XRD patterns. After 60hr milling, the solid solution has been largely formed and a significant decrease in the intensities of the diffraction lines can be observed. The broadening of the peaks as shown in Figure 37 is commonly attributed to the structural change in the samples, such as the formation of amorphous phases, large lattice strains in grains, or the embedding of very small crystals in an amorphous matrix[15].

Figure 36 Fe and Cr impurities in milled powders.

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Figure 37 XRD patterns of Ni-Ti powders after mechanical alloying for various periods of time

From Figure 35 to Figure 37, it can be observed that the particle size of the powder may have a significant effect on the wear behaviour of the steel milling media. During the initial 75hr milling, abrasive wear of the steel milling media should be the main wear mechanism due to the relatively large particle size of powders. After 75hr milling, the powder size becomes much smaller and the powders tend to stick onto the balls during the milling process. The significant increase in the impurity levels of Fe and Cr after 75hr may be due to the adhesive wear of the milling media. Consequently, 75hr is the optimum time for the mechanical alloying of nanocrystalline Ni-Ti with least impurities. Further milling will increase the amount of impurities in the powders significantly.

5.4.2 Effect and Result of Mechanical Alloying Ti-Si

The surface morphologies and the change of particle size of Ti-Si powders at different milling times are shown in Figure 38. After ball milling, a reduction of particle size can be observed (Figure 38b-c). With further milling, the powders become more homogeneous while keeping the granular morphology (Figure 38d-f). The particle size is smaller than 1 μm after 120hr milling. Agglomeration of particles in large aggregates can be observed after 30hr milling.

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Figure 38 SEM micrographs of $\text{Ti}_{86.5}\text{Si}_{13.5}$ powder at different milling times. (a) 0; (b) 5; (c) 10; (d) 30; (e) 60; (f) 120 h.

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Figure 39 shows the XRD patterns of Ti-Si powders as a function of milling time, revealing the structural evolution as milling progressed in the powder mixture. With an increase in the milling time, the peaks of Ti and Si gradually broaden and the intensities of peaks decrease. Ti peaks shift towards the higher diffraction angles after longer milling time.

Figure 39 XRD patterns of Ti-Si powder mixtures at various stages of mechanical alloying.

For the as-mixed elemental blends, the XRD patterns show the presence of individual elemental Ti with hexagonal close packed (h.c.p.) phase and Si with cubic phase, as shown in Figure 39. The intensity of Si peaks decreases with increasing milling time. After 60hr milling, the Si peaks disappear from the XRD pattern and only peaks of Ti solution can be seen. This indicates that Si has either become amorphous or fully dissolved into Ti, i.e., the starting Ti-Si powders have transformed into Ti supersaturated solid solution Ti(Si). Figure 40 shows the change of position and shape of Ti (100) and Si (111) diffraction peaks at the selected milling times.

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Figure 40 Change of position and shape of diffraction peaks after selected milling times. (a) Ti(100); (b) Si(111).

The Ti peaks are observed to shift towards the higher diffraction angles, indicating the dissolution due to interdiffusion between the two elements during milling. However, no obvious shifts are detected for the Si peaks, indicating less dissolution of Ti in Si due to the fact that the atomic radius of Ti is larger than that of Si. The above results indicate the formation of an inhomogeneous solution of Si in Ti. Considering the fact that ball milling on pure Ti produces only the peak broadening for this reflection, the peak shift towards the higher angle direction as milling continues can be attributed to the change in the lattice parameters due to the diffusion of Si into Ti. Figure 41 and Figure 42 show the lattice parameter c/a (calculated from XRD results) and cell volume V as a function of the milling time.

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Figure 41 Lattice parameters and unit cell volume vs. milling time. Lattice parameters

Figure 42 Lattice parameters and unit cell volume vs. milling time. Lattice parameter ratio c/a and unit cell volume V .

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Before mechanical alloying, the lattice parameter ratio c/a of h.c.p. Ti phase is 1.5852, which is close to the theoretical h.c.p. lattice parameter ratio. After milling for 45hr, the c/a ratio and cell volume do not show apparent changes. The decrease of the ratio c/a indicates that atoms of Si occupy some positions in the h.c.p. lattice of Ti during the process of mechanical alloying, causing the Ti lattice to shrink. Further milling to 60hr results in a significant decrease in c/a ratio to 1.5385. The cell volume also decreases from the original 0.0352 nm^3 to 0.0329 nm^3 . Beyond 60 h milling, the c/a ratio and cell volume tend to stabilize around 1.5341 and 0.0328 nm^3 (calculated values) respectively. This suggests that the alloying between Ti and Si mainly takes place before 60hr milling and the formation of Ti(Si) solid solution has completed at about 60hr. Suryanarayana [2] also reported that the supersaturated solid solution was formed at the early stage of milling process. Velt et al.[116] suggested that the energy stored in the grain boundaries served as a driving force for the formation of a solid solution. A substantial amount of enthalpy can be stored in nanocrystalline metals due to the large grain boundary area as the crystallite size of elemental components decreases [117]. From the equilibrium phase diagram of Ti-Si system, it is known that Si practically does not dissolve in Ti lattice at lower temperatures. The equilibrium solubility of Si in Ti lattice is only 0.5 at.% [117]. The solubility of Si in Ti increases significantly due to the high-energy ball milling. By applying the lattice parameters of Ti, Si and Ti(Si) at different milling times, the solubility of Si in Ti lattice at different milling times can be obtained from the Vegard's Law, as shown in Figure 43.

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Figure 43 Solubility of Si in Ti lattice as a function of milling time.

It can be observed from Figure 43 that the solubility of Si in Ti lattice is lower than 2 at.% at 20 h milling. The solubility increases significantly after 20hr milling. It reaches a value of 12.72 at.% after 60hr milling and the solubility almost remains the same with the further increase in milling time. This indicates that most of the Si atoms are dissolved into the Ti lattice and a small amount of remaining undissolved Si becomes the amorphous phase during mechanical alloying.

The broadening of the peaks is commonly attributed to the structural change in the samples, such as the formation of amorphous phases, large lattice strains in grains, formation of extremely fine particles, or the embedding of very small crystals in an amorphous matrix [117]. The weakening and broadening of the Ti and Si peaks indicate the substantial decrease in the grain size during mechanical alloying. The broadening of diffraction peaks due to the decrease of crystallite size is given by the Scherrer equation [118],

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$$\beta = \frac{0.9\lambda}{D \cos \theta}$$

Equation 5-12

where β is the peak width in radians at half maximum intensity, λ is the wavelength of the X-ray used, D is the crystallite size, and θ is the diffraction Bragg angle. Based on this equation, the calculated average crystallite size of Ti and Si powders as a function of milling time is shown in Figure 44.

Figure 44 Crystallite size of mechanically alloyed Ti-Si powders as a function of milling time.

Upon milling, the crystallite sizes of Ti and Si decrease with increasing milling time. After 60 h milling, the Si peaks disappear from the XRD patterns and the crystallite sizes inferred from Ti (101), (100) and (002) peaks are in the range of between 5 and 15 nm. With a further increase in the milling time after 60hr, the crystallite size remains almost the same. It must be noticed that both the reduction in crystallite size and the introduction of internal strain during mechanical alloying can produce the broadening of spectral

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peaks simultaneously. The calculated crystallite sizes are probably therefore underestimated because of the fact that the contribution of micro-strains to the peak broadening has been neglected.

To verify that the crystallite size is in the nano-sized scale, TEM observations of Ti-Si synthesized by mechanical alloying for 120hr have been performed and the results are shown in Figure 45a. The TEM micrograph confirms that the presence of nanocrystalline Ti-Si after mechanical alloying for 120hr. The selected area diffraction (SAD) rings as shown in Figure 45b confirm that the powder is predominantly nano-polycrystalline structure with traces of the remnant amorphous phase. This is consistent with the studies by Yang et al. [29], who reported that the metastable solid solution phases should form rather than the amorphous phases when Ti composition was higher than 78%.

(a) Bright field image of milled powder   (b) SAD pattern

Figure 45 TEM observation of 120h-milled powder.

Energy dispersive spectroscopy (EDX) depicts that the composition of the milled powders contains Ti, Si and Fe and Cr impurities. Figure 46 summarizes the Fe and Cr impurity content at different stages of milling. There is only a small amount of impurities at the initial milling stage of 60hr. The content of impurity increases at the final stage and approaches a saturation beyond 90h. At 60hr milling, the impurity contents of Fe and Cr are 2.5 and 0 at.% respectively, while 8.7 at.% Fe and 1.4 at.% Cr are obtained after 120h milling. The main source of Fe and Cr impurities is the abrasive

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wear debris of the steel milling media (vial/balls) throughout the milling process. The particle size of the powder is found to have a significant effect on the abrasive wear of the steel milling media.

Figure 46 Chemical analysis of impurities at different stages of milling

5.5 Sintering

Ti-6Al-4V material was manufactured through the traditional sintering process, with as-received powder and with alloyed powder. Sintering of the powder was done together for both the milled and as-received powder in the Oxy-gon furnace in a vacuum environment. The powders were mixed in the ratio of 90% of titanium, 6% of aluminium and 4% of vanadium.

The Ti-Si-Zr and Ti6Al4V will be produced through the traditional synthesis process. Ti6Al4V will be sintered, as a reference material to the Ti-Si-Zr. The investigation was carried out using different particle sizes of Titanium and Silicon. MA of Ti-Si with the addition of 7.14 at. % of Zirconium powders (addition of this element is to lower the Young's modulus) and Titanium. All three elements will be mixed in variation in the percentage of content. After mixing, the contents will be compacted into a green density and pre-heated to a certain temperature. Temperature control of the mixture will vary

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(transient liquid phase (Eutectic point) with four different setting during sintering. Environment used will be vacuum. Addition of the zirconium is inorder to lower the Young's modulus of the formed material. Sintering will be carried out with and without the addition of TiH_2 as comparison can be made between the two mixes.

Without the addition of TiH_2 the sintering rate will follow the guideline from the reference material. With addition of TiH_2 the sintering will be from 0°C to 500°C at a rate of $5^\circ\text{C}/\text{min}$ and 500°C to 1200°C the ramp rate will increased to $20^\circ\text{C}/\text{min}$ respectively.

Powder mixture of 3 grams was taken from the vial every two hours and similarly relative weight of balls were removed to maintained the charge ratio of 15:1. The following Figure 38a to Figure 38f showed the series of milled powder taken from the jug under the SEM.

5.5.1 Sintering of Ti6Al4V

Sintering of Ti6Al4V as a reference material for Ti-Si-Zr . Pressure 0.7023MPa (compaction force) sintering at 950°C holding 4hr drop to 0°C in 3hrs heat up to 1100°C drop to room temperature.

Figure 47 Ti6Al4V Sintered sample with high porosity formed

Figure 48 Ti6Al4V Sintered sample formation of necking can be noticed

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Figure 49 Ti6Al4V at higher magnification

Figure 50 Ti6Al4V at higher magnification

Figure 50 of the EDX results show the atomic composition of Figure 49, which suggested that α - β Titanium are formed due to the rapid rise of the high sintering temperature up to 1100°C and slow cooling to room temperature. From Figure 48 the sintering process was at the first and second stage of sintering because the particles size of the powders were still visible. For sintering of titanium done by Oh el at[57] at about 1200°C with 374 μ m powder formed melts and necking took place between the powder.

Figure 51 Sintering of Titanium powder with melts forming and necking taking place[57]

This suggested that the German's theory of sintering (See Figure 29) was taking place. Formation of a small amount of liquid on the surface and between the surface powders which promotes the following possible reaction[79]:

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- Evaporation condensation
- Surface diffusion
- Volume diffusion
- Plastic diffusion
- Plastic flow
- Grain bounding

Therefore Figure 51 shows the melting within the interparticles contact points. Leading to the pore formation, which is calculated with the image analysis yielding 60% of porosity.

The above mentioned sintering temperature and parameters was over the β -transus transformation temperature along a relatively slow cooling rate. The result of such sintering parameters will result in formation of α - β titanium to be formed. Researchers like Smugeresky et al[119] found that by slowly cooling through the β -transus temperature blocky α -plates with intergranular- β were formed. It is similar to the parameters for sintering of Ti6Al4V material. With the addition of vanadium as the β stabilizer thus the sintering of α - β titanium was(will be) formed.

5.5.2 Sintering of Ti-Si-Zr without Addition of TiH₂ as a foaming agent

The Ti-Si-Zr powders are prepared with the following respective conditions. The Ti and Si powders were alloyed at eutectic composition (point) and mixed with the pure elementary powder of Ti and Zr.

Figure 52 to Figure 54 show the SEM morphology of as-received powder. Sintering of the Ti-Si-Zr was carried out from 1000°C ~1200°C as from the phase diagram for Ti-Si.

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Figure 52 Titanium elemental powder –
200mesh

Figure 53 Silicon elemental powder +325mesh

Figure 54 Zirconium elemental powder –200mesh

From Figure 55 DTA result, it determined the temperature driving sintering process. As the peak goes below the zero mark show the absorption of the heat during the test. At about 700°C plus degrees show another absorption of the heat energy is observed. This shows the formation of the liquid phase during that temperature.

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Figure 55 DTA result of Mechanical alloyed of Ti-Si

The sintering process was carried out and the phase analysis was identified by Ti-Zr-Si ternary phase diagram in Figure 161

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Ti-Si-Zr mix sintered at 1500°C with 1ton force

According to the phase diagram, the sintering temperature was set at 1500°C and the below figures shows the results for the sintered samples. Figure 56 shows the sample compacted at 1ton pressure.

Figure 56 Ti-Si-Zr mix sintered at 1500°C with 1ton force x1000

Figure 57 Whole Area Ti 30.60 Si 34.79 Zr 34.61

From Figure 56 and Figure 57 the SEM showed that small pores were formed at this sintering temperature, which suggested that the liquid formation was excessive thus causing most of the pores to be isolated from each other. The formation of too much liquid at 1500°C also caused the formation of an intermetallic, which is visible from Figure 56 with the backscattering mode used (See Table 10). The presence of the intermetallics makes the material hard and brittle at these instances. In addition, it encourages small pore formation and a non-uniformed distribution throughout the samples.

Table 10 EDX analysis of the points of Figure 57

Point	Titanium (Ti)	Silicon (Si)	Zirconium (Zr)	Iron (Fe)	Chromium (Cr)
1	30.60	34.79	34.61	nil	nil
2	83.52	3.77	12.71	nil	nil
3	69.45	3.87	13.55	11.57	1.57
4	84.89	3.62	11.49	nil	nil

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Ti-Si-Zr mix sintered at 1500°C with 2ton force

From Figure 58 and Figure 59 it can be seen that the pores formed are both small and secluded suggesting that too much melt has formed at the temperature of 1500°C. Excessive melt and high temperature also causes the formation of the undesirable brittle phase which has been observed from the EDX results (Figure 59 see Table 11).

Table 11 EDX analysis of the points of Figure 58

Point	Titanium (Ti)	Silicon (Si)	Zirconium (Zr)	Iron (Fe)	Chromium (Cr)
1	80.60	4.79	14.61	Nil	nil
2	85.43	3.21	11.36	Nil	nil
3	33.91	38.01	28.09	Nil	nil

Figure 58 Ti-Si-Zr mix sintered at 1500°C with 2ton force x1000

Figure 59 Ti-Si-Zr mix sintered at 1500°C with 2ton force x2000

Ti-Si-Zr mix sintered at 1500°C with 3ton force

Sintering at similar temperature but compacted with 3-ton pressure (Figure 60), the pores formed are relatively small. The pores were closed suggesting that a large amount of liquid was formed (see Figure 61). Similar to the 1 and 2-ton samples, intermetallics are

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formed along with their respective mechanical and metallurgical properties (See Table 12).

Table 12 EDX analysis of the points of Figure 61

Point	Titanium (Ti)	Silicon (Si)	Zirconium (Zr)	Iron (Fe)	Chromium (Cr)
1	31.34	31.71	36.87	nil	nil
2	82.72	3.85	13.45	nil	nil
3	83.20	4.29	21.51	nil	nil
4	83.20	3.90	12.58	nil	nil

Figure 60 Ti-Si-Zr mix sintered at 1500°C with 3ton force x1000

Figure 61 Ti-Si-Zr mix sintered at 1500°C with 3ton force x2000

Ti-Si-Zr mix sintered at 1500°C with 5ton force

Figure 62 displayed once more small and closed pores formed when sintering at 1500°C with a compaction pressure of 5-ton. EDX analyses were carried out as show in Figure 63. Several intermetallic phases were formed (see Table 13).

Table 13 EDX analysis of the points of Figure 63

Point	Titanium (Ti)	Silicon (Si)	Zirconium (Zr)	Iron (Fe)	Chromium (Cr)
1	84.11	3.48	12.41	nil	nil
2	31.68	36.68	32.08	nil	nil
3	87.01	3.39	9.29	nil	nil
4	64.06	17.64	18.30	nil	nil

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Figure 62 Ti-Si-Zr mix sintered at 1500°C with 5ton force

Figure 63 Ti-Si-Zr mix sintered at 1500°C with 5ton force

With pressure applied (for compaction to form green body) at 1, 2, 3 and 5ton and a sintering temperature of 1500°C the pores formed were small, poorly distributed and either isolated or closed. Thus it can be concluded that 1500°C is not suitable for the Ti-Si-Zr mix. In addition, the formation of intermetallics was undesirable. The use of a foaming agent to aid in the formation of pores will be discussed in the next section.

5.5.3 Sintering of Ti-Si-Zr with Addition of TiH_2 as a foaming agent

The sintering rate is the key to the formation of the pores when using TiH_2 , as the application of a foaming agent during sintering. The sintering temperatures were carried out at 885, 940, 1000, 1050 and 1200°C at each sintering temperature a sintering rate of 20 and 30°C/min are used. Two mixes of TiH_2 (40% and 80%) along with 2 different particles (43 and 500µm) were used (see Figure 64 and Figure 65).

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Figure 64 SEM morphology of TiH₂ of 43µm   Figure 65 SEM morphology of TiH₂ of 500µm

DTA was carried out on the TiH₂ (See Figure 66). During the test at about 635°C the decomposition of the TiH₂ to titanium (Ti) hydrogen (H) occurred, which would result in the formation of the pores.

Figure 66 DTA results of TiH₂

Ti-Si-Zr mix sintered at 885°C with 1ton force with 40% TiH₂ (43µm) and at 20°C/min heating rate

In Figure 68, the three points of different material contrast are identified, EDX was carried out at these locations and the results are presented in Figure 69 to See Appendix page 200 reveals a high concentration of zirconium present (57.69 at. %) and with

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titanium dissolving with it along with some silicon. Point 2 is the grey region with the presence of silicon and titanium, which is the MA powder of Ti-Si with concentration of Ti 94.41 and Si of 5.41 at. % (see Appendix page 200). Point 3 the was high in concentration of Ti 99.88 at % and little traces of zirconium present (see Appendix page 200)

Figure 67 Ti-Si-Zr mix sintered at 885°C with 1ton force with 40% TiH2 (43µm) and at 20°C/min heating rate

Figure 68 Ti-Si-Zr mix sintered at 885°C with 1ton force with 40% TiH2 (43µm) and at 20°C/min heating rate

Figure 69 Whole Area Ti 94.81 Si 2.03 Zr 3.16

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Ti-Si-Zr mix sintered at 885°C with 1ton force with 80% TiH₂ (43µm) and at 20°C/min heating rate

Figure 70 shows a SEM picture of Ti-Si-Zr sintered at a higher sintering rate of 30°C/min and Figure 71 showed a close up view of the pore formed. Figure 71 shows the EDX analysis of the region indicating the relative composition present. For point 1 the white areas displayed a high concentration present of zirconium (i.e. 69.39 at. %) and titanium content of 30.61 at. % (see Appendix page 201). Point 2 is the MA powder of Ti-Si melting at the outer boundary with presence of little zirconium (see Appendix page 201 for the at %).Point 3 has a high concentration of titanium up to 98.27 at. %, and zirconium of 1.73 at. %.(see Appendix page 201)

Figure 70 Ti-Si-Zr mix sintered at 885°C with 1ton force with 40% TiH₂ (43µm) and at 20°C/min heating rate

Figure 71 Ti-Si-Zr mix sintered at 885°C with 1ton force with 40% TiH₂ (43µm) and at 20°C/min heating rate

Figure 72 Whole Area Ti 91.10 Si 1.76 Zr 7.14

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Ti-Si-Zr mix sintered at 940°C with 1ton force with 40% TiH₂ (43µm) and at 20°C/min heating rate

Increasing the sintering temperature should result in the creation of more pores however, it will also lead to increased intermetallic formation. According to the phase diagram, at a temperature of 940°C, the melting of the MA powder will take place and this will cause the gluing of the pure Ti and Zr together. The addition of TiH₂ will assist in the pore formation as observed in Figure 73. Figure 74 shows where the EDX analysis was carried out. The analysis shown in Figure 75 is of the general content mix of Ti 91.10, Si 1.76 and Zr 7.14 at. %. Point 1 shows a high concentration of Zr of 65.19 and Ti of 34.81 at. %. (see Appendix page 202) shows the presence of MA powder melting and moving towards the Ti or Zr powders. Point 3 (the dark region) (see Appendix page 202) shows pure Ti of concentration of 99.01 at. %

Figure 73 Ti-Si-Zr mix sintered at 940°C with 1ton force with 40% TiH₂ (43µm) and at 20°C/min heating rate

Figure 74 Ti-Si-Zr mix sintered at 940°C with 1ton force with 40% TiH₂ (43µm) and at 20°C/min heating rate

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Figure 75 Whole Area Ti 91.10 Si 1.76 Zr 7.14

Ti-Si-Zr mix sintered at 940°C with 1ton force with 80% TiH₂ (43μm) and at 20°C/min heating rate

Figure 76 show the sample sintered at 940°C with a similar heating rate of 20°C/min but with 80% content of TiH₂, which exhibits a rather porous structure. Figure 77 shows the EDX was carried out in the marked areas. Figure 78 shows a general analysis of the sample giving a Ti 90.39, Si 3.40 and Zr 6.21 at. %. At point 1 the content of Zr was a high concentration of 52.16 at. %. At point 2 the presence of the MA powder was observed from the analysis showed (Ti 85.25 Si 14.38 Zr 0.35 and Fe 0.03 at. %). The dark area at point 3 (in see Appendix page 203) showed the presence of pure Ti with 99.33 at. %.

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Figure 76 Ti-Si-Zr mix sintered at 940°C with 1ton force with 80% TiH₂ (43μm) and at 20°C/min heating rate

Figure 77 Ti-Si-Zr mix sintered at 940°C with 1ton force with 80% TiH₂ (43μm) and at 20°C/min heating rate

Figure 78 Whole Area Ti 90.39 Si 3.40 Zr 6.21

Ti-Si-Zr mix sintered at 1000°C with 1ton force with 40% TiH₂ (43μm) and at 20°C/min heating rate

As the sintering temperature increases, the surface morphology changes, in Figure 79, the pores formed are smaller and closed up. This is evidenced by the decrease in height and diameter (this will be mentioned later-see Figure 106 to Figure 113). In the backscattered image, the material contrast shading has changed suggesting different elements are found within the system. A general EDX analysis was carried out within the area showing content of Ti 87.53, Si 4.67 and Zr 7.80 at. %.

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Figure 79 Ti-Si-Zr mix sintered at 1000°C with 1ton force with 40% TiH₂ (43µm) and at 20°C/min heating rate

Figure 80 Ti-Si-Zr mix sintered at 1000°C with 1ton force with 40% TiH₂ (43µm) and at 20°C/min heating rate

Figure 81 Whole Area Ti 87.53 Si 4.67 Zr 7.80

Ti-Si-Zr mix sintered at 1000°C with 1ton force with 80% TiH₂ (43µm) and at 20°C/min heating rate

Sintering with the higher content of TiH₂ the number of pores formed did not increase, and closed pores are formed. The general EDX analysis showed there were Ti 87.65, Si 3.39, Zr 7.98 and Fe 0.97. This showed there are intermetallics formed as iron impurity was detected by the backscatter. These iron impurities were attributed the previously milling process of Ti-Si powder for 75hrs

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Figure 82 Ti-Si-Zr mix sintered at 1000°C with 1ton force with 80% TiH₂ (43μm) and at 20°C/min heating rate

Figure 83 Ti-Si-Zr mix sintered at 1000°C with 1ton force with 80% TiH₂ (43μm) and at 20°C/min heating rate

Figure 84 Whole Area Ti 87.65 Si 3.39 Zr 7.98 Fe 0.97

Ti-Si-Zr mix sintered at 1050°C with 1ton force with 40% TiH₂ (43μm) and at 20°C/min heating rate

At a temperature of 1050°C the pores formed were not sufficient in number or size. One remedy could be the use of the larger TiH₂ particles for example 500μm (see Figure 85). The general phase formed is Ti 90.84 Si 4.36 Zr 4.80 (see Figure 87).

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Figure 85 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 40% TiH₂ (43µm) and at 20°C/min heating rate

Figure 86 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 40% TiH₂ (500µm) and at 20°C/min heating rate

Figure 87 Whole Area Ti 90.84 Si 4.36 Zr 4.80

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Ti-Si-Zr mix sintered at 1000°C with 1ton force with 40% TiH₂ (500μm) and at 30°C/min heating rate

Figure 88 shows the SEM of a sample sintered at 1000°C with TiH₂ of 40% by weight and with heating rate of 30°C/min. In Figure 89 the clear contrast of the different metals can be seen. EDX analysis was carried out on the different regions. Figure 90 shows the analysis of the general area with content of Ti 79.82, Si 8.17 and Zr 12.01 at. %. Point 1 (in see Appendix page204) shows a relative high content of Zr of 27.08 and Ti at 71.63 at % with traces of Si present. Point 2 (in see Appendix page 204) shows the diffusion of MA Ti-Si into the Ti particles. While point 3 shows pure Ti present (97.49 at. %)(see Appendix page 204)

Figure 88 Ti-Si-Zr mix sintered at 1000°C with 1ton force with 40% TiH₂ (500μm) and at 30°C/min heating rate

Figure 89 Ti-Si-Zr mix sintered at 1000°C with 1ton force with 40% TiH₂ (500μm) and at 30°C/min heating rate

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Figure 90 Whole Area Ti 79.82 Si 8.17 Zr 12.01

Figure 91 shows a similar sintering as in Figure 88 with first and second stage of sintering taking place at this temperature. Oh et. al[57] sintered porous Ti and as they mentioned some of the samples could not be polished as they were falling apart as the grinding or polishing was taking place. Similar here the sintered sample fell off during grinding or polishing. With the increase of TiH_2 to 80% by weight and the increase in heating rate, the pore formation was relatively similar in both of the sintered samples. Figure 92 shows the points where EDX was undertaken on this sample. Figure 93 shows a general concentration of Ti 86.28, Si 7.35 and Zr 6.37 at. %. (see Appendix page 205) has a high concentration of Zr present of 39.86 with Si 9.28 and Ti 50.85 at. %. (see Appendix page 205) analysis shows the presence of the MA powder of Ti-Si melting and moving inwards similar to what was seen earlier (see Appendix page 205). See Appendix page 205 shows a content of high concentration of Ti 98.64 at. % present with little of Zr of 1.36 at. %

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Figure 91 Ti-Si-Zr mix sintered at 1000°C with 1ton press with 80% TiH_2 (500 μm) and at 30°C/min heating rate

Figure 92 Ti-Si-Zr mix sintered at 1000°C with 1ton press with 80% TiH_2 (500 μm) and at 30°C/min heating rate

Figure 93 Whole Area Ti 86.28 Si 7.35 Zr 6.37

Ti-Si-Zr mix sintered at 1050°C with 1ton force with 40% TiH_2 (500 μm) and at 20°C/min heating rate

Figure 94 illustrates that it has shown the best porosity in terms of size distribution and interconnectivity of the samples (so far) after sintering at 1050°C. The phase formed can be clearly seen in Figure 95. The general EDX analysis of the sample shows (Figure 96) 83.37 of Ti, 5.61 of Si and 11.03 of Zr (all in atomic percentage). The white areas generally contained Zr and Ti which formed an intermetallic mix of β -Zr (according to the phase diagram). The grey region formed a mix of Ti-Zr with a higher content of

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titanium in it. Point 3 of the dark region showed the pure titanium with concentration up to 97.63 at. %(see Appendix page 206)

Figure 94 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 40% TiH₂ (500µm) and at 20°C/min heating rate

Figure 95 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 40% TiH₂ (500µm) and at 20°C/min heating rate

Figure 96 Whole Area Ti 83.37 Si 5.61 Zr 11.03

Ti-Si-Zr mix sintered at 1050°C with 1ton force with 80% TiH₂ (500µm) and at 20°C/min heating rate

With a higher content of TiH₂ there should be a corresponding increase in porosity found in the sintered samples. However Figure 97 shows similar results to those observed (Figure 94). The general EDX in Figure 99 shows contents of Ti 81.5, Si 7.64 and Zr

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11.04 at. %. Point 1 region is a intermetallic mixed with the iron present due to the contamination from the mechanically alloying of Ti-Si process. Point 2 (see Appendix page 207) the grey region formed the β -Zr with sintering temperature reaching 1050°C. Point 3 (see Appendix page 206) the dark region represent a high concentration of Ti and it was suspected that pure titanium was present there.

Figure 97 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 80% TiH₂ (500µm) and at 20°C/min heating rate

Figure 98 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 80% TiH₂ (500µm) and at 20°C/min heating rate

Figure 99 Whole Area Ti 81.5 Si 7.46 Zr 11.04

Ti-Si-Zr mix sintered at 1050°C with 1ton force with 40% TiH₂ (500µm) and at 30°C/min heating rate

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The increase in sintering rate with the intention of achieving a greater number of pores is shown in Figure 100 not to have been successful. Figure 102 showed a general EDX of Ti 83.23, Si 8.54 and Zr 8.23 similar to the findings reported by of Salpadoru et al[120]. Point 1 analysis is with higher concentration of silicon and zirconium, which is Ti 39.74, Si 27.15 and Zr 32.75 at. %. This showed an intermetallic region and in point 2 a relative similar analysis from EDX are as follows Ti 50.61, Si 21.21 and Zr 28.18. From point 3 dark region is a concentration of titanium up a high of 97.52 of Ti and the rest are made of Zr (2.48 at. %) (see Appendix page 208)

Figure 100 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 40% TiH₂ (500µm) and at 30°C/min heating rate

Figure 101 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 40% TiH₂ (500µm) and at 30°C/min heating rate

Figure 102 Whole Area Ti 85.23 Si 8.54 Zr 6.23

Ti-Si-Zr mix sintered at 1050°C with 1ton force with 80% TiH₂ (500µm) and at 30°C/min heating rate

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Sintering was carried out at 1050°C temperature again but with a higher heating rate at 30°C/min to hasten the pore formation. The higher rate will allow the decomposition of hydrogen from the TiH_2 . From the SEM Figure 103 it seems that the material peels off while grinding or polishing the sample (similar reporting by Oh et. al[57]) where some of the sintered porous Titanium can not be polished or grinded. No doubt there are small little pores present (as seen in the Figure 103). Figure 104 shows the EDX analysis conducted at the marked points. The general compositional analysis is shown in Figure 105. Has some interesting analysis of the melting of the MA powder of Ti-Si evident because of the presence of a small amount of iron (see Appendix page 209). This impurity was inherited from the ball milling process. Point 2 shows the presence of the Zr in a relative high content of 18.8 at. % (see Appendix page 209). Point 3 shows pure titanium with concentration of 99.59 at. % (see Appendix page 209).

Figure 103 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 80% TiH_2 (500μm) and at 30°C/min heating rate

Figure 104 Ti-Si-Zr mix sintered at 1050°C with 1ton force with 80% TiH_2 (500μm) and at 30°C/min heating rate

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Figure 105 Whole Area Ti 93.61 Si 1.3 Zr 4.32 Fe 0.77

5.5.4 Sintering Effect of Addition of TiH_2

From the earlier experiments carried out, the pores formed were little (10-20% porosity level), not well distributed and were too small (10-15 μm). Therefore bigger (100 μm) and more numerous pores (40%) are needed to be produced during the sintering process. This section will concentrate on the effect on pore formation of TiH_2 and, in particular, the dimensional change after sintering has been carried out

Diameter Shrinkage(TiH_2 43 μm)

Pore shrinkage (when compared to the original green compact) has occurred. By increasing the sintering temperature and sintering rate, the compacted samples decreased in height. While increasing the temperature from 940°C to 1000°C the dimensional shrinkage increased from 3% to 9%. Similar observations were seen in Figure 106 to Figure 109. Sintering of the samples were based on temperature driven concepts so as controlling the sintering temperature can control the amount of liquid phase formation and omitting the intermetallic formation or the brittle phases, which are likely to be formed if too much of liquid phase were formed.

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Figure 106 Percentage of diameter Shrinkage with 40% of TiH₂ (43μm) at 20°C/min sintering rate

Figure 107 Percentage of diameter Shrinkage with 80% of TiH₂ (43μm) at 20°C/min sintering rate

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Figure 108 Percentage of diameter Shrinkage with 40% of TiH₂ (43µm) at 30°C/min sintering rate

Figure 109 Percentage of diameter Shrinkage with 80% of TiH₂ (43µm) at 30°C/min sintering rate

In the next set of samples the mixes of TiH₂ was increased to 80wt. %. Raising the content of TiH₂ within the compact and elevating the sintering rate causes (for example most of the sample to shrink in a rapid and significant dimensional change of diameter and height). As the heating rate increases, the TiH₂ is decomposed into Titanium and

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Hydrogen. During heating or the heat treatment process, an oxide layer forms on the surface of the hydride and slower diffusion of hydrogen through this oxide is thought to retard the hydrogen release[121]. If within the molten metal, the layer of oxide could be easily broken down and therefore allowing the release of hydrogen atom. Only a small amount of hydrogen was released causing the small pore formation however, the samples shrunk because too much liquid phase was formed. The project chose to work with a transient liquid phase sintering process with a little wetting taking place and quick rearrangement. There is not a large amount of liquid formed and therefore pores formed were small which will be discussed later. If too much of the liquid phase was formed there will be a considerable inter-diffusion within the sample. In similar cases, too much wetting taking place will cause the pores formed in the initial stage of sintering to close up and become isolated pores. The aim of the project was to engineer pore creation. The transient liquid phase will assist the sintering in forming little liquid along the contacts points of the powder. This allows the grain boundary diffusion to occur and omits the formation of the brittle phase. Unlike the work carried out by Kennedy et al.[122], who experimented with as little as 3 vol. % of particles and foaming the material to several hundred times of its original dimension. In the process of foaming the material, they indeed created large pores and the height of the samples grew significantly. For that research the work on wetting was significant with micrographs of the foams illustrated Al_2O_3 , SiC and TiB_2 embedded within the wall of the foams. The work by Kennedy et al. was different as they created the liquid phase sintering which is different from our research as we are concerned with transient liquid phase sintering. Kennedy sintering the material to molten state and the release of the hydrogen from the hydride was continuous and therefore big pores were formed which indirectly changed the height of the sample significantly. In this work of transient liquid phase sintering there was little liquid formed (due to the fact that the research was base on TPLS) and hydrogen release was not continuous leading to little or shrinkage in height after sintering.

Sintering by varying parameters such as heating rate, sintering temperature and TiH_2 content was reported by Li et al[77] who had similar results. The material height's before and after sintering was different, as the height increased to about 50 to 100%. However this work was restricted to working with only high sintering temperature and low content of TiH_2 . In our research, additional variable such as TiH_2 particle size and heating rate are considered.

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Height Shrinkage(TiH₂ 43μm)

The relative shapes of the samples were retained but results for the percentage of height shrinkage were similar to that of the diameter shrinkage. With an increase in sintering temperature the decrease of the height was linear. The same trends were noted for an increase in the content of TiH₂ and sintering rate.

Sintering temperature increases the decomposition of TiH₂ at 635°C from the DTA results. This decomposition of TiH₂ is quite exothermic which triggers the release of hydrogen and released newborn titanium in the system. The newborn Ti will react with other powders like Zr or alloyed powders of Ti-Si present. This will cause contraction of the samples with the increase in the sintering temperatures. At this stage of sintering the incomplete decomposition of TiH₂ will react with any of the powder with the compact such as, example the MA Ti-Si (See Figure 94 of SEM picture). When the sintering temperature was high (at about 1050°C) the sample did not turn into molten stage. For TiH₂ to create the foam and release hydrogen from the Titanium hydride, the molten stage must be achieved as reported by Kennedy et al[123].

Figure 110 Percentage of Height Shrinkage with 40% of TiH₂ (43μm) at 20°C/min sintering rate

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Figure 111 Percentage of Height Shrinkage with 80% of TiH₂ (43μm) at 20°C/min sintering rate

Figure 112 Percentage of Height Shrinkage with 40% of TiH₂ (43μm) at 30°C/min sintering rate

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Figure 113 Percentage of Height Shrinkage with 80% of TiH₂ (43μm) at 80°C/min sintering rate

Likewise the TiH₂ was decomposed during sintering, but the small amount of liquid phase sintering was present but not enough to fully decompose the titanium hydride. Therefore the height shrinkage was relatively identical for all the samples and was about 14% shrinkage in size. The sintering temperature is not high enough and therefore it is preventing the formation of large amount of liquid. Consequently, the shrinkage for the height and diameter was relatively similar and inevitable. As sintering temperature was not high, only a little wetting occurred, as it was concentrated between the grains of the powders or inter-contact points. At the contact points with only a small amount of liquid present only surface and grain boundary diffusion was, according to German[79] likely to occur.

Diameter Shrinkage (TiH₂ 500μm)

Figure 114 to Figure 116 show the dimensional percentage shrinkage in relation to temperatures. For the sintering temperature of 940°C an expansion in diameter has occurred while for all other temperatures the opposite is noted. This support earlier findings with shrinkage attributed to the little amount of liquid formed during sintering which causes the TiH₂ to form an oxide layer on the surface of the hydride during the initial heating process[124], and thus retard the diffusion of hydrogen and hinder the rate

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of release of the hydrogen atom from it[121]. If the sample was heated to molten form, this will result in the TiH_2 reacting and releasing the hydrogen atom easily but this will also result in the formation of the undesirable intermetallic.

Figure 114 Percentage of diameter Shrinkage with 40% of TiH_2 (500 μm) at 20°C/min sintering rate

Figure 115 Percentage of diameter Shrinkage with 80% of TiH_2 (500 μm) at 20°C/min sintering rate

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Figure 116 Percentage of diameter Shrinkage with 40% of TiH₂ (500μm) at 30°C/min sintering rate

Figure 117 Percentage of diameter Shrinkage with 80% of TiH₂ (500μm) at 30°C/min sintering rate

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In this comparison of the diameter, from Figure 114 to Figure 116 the sintering temperature was at 885°C exhibit the expansion of the diameter. Other sintering temperatures of 940°C to 1050°C from Figure 114 to Figure 116 show shrinkage occurring similar to the earlier reported in pages 159 with samples sintered 940°C.

Working with transient liquid phase sintering only a small amount of liquid is formed while sintering (at the determined temperature from the phase diagram). The melts start at the inter-contact points of the compacted powder. Surface and boundaries diffusion takes place as proposed by German[53](see Figure 29 for an example). The small amount of liquid formed triggers the release of the hydrogen from TiH_2 and pores are formed.

Height (TiH_2 500 μm)

In Figure 118 to Figure 121 the specimen clearly expanded instead of contracting at the sintering temperature of 885°C. Therefore, there was an expansion of the pores after sintering compared to the original green compact dimensions and what had taken place after sintering (i.e height changes). As suggested by Fujita et al[97] the formation of a small amount of liquid takes place when melting of Ti-Si occurs at 700 degrees plus. As the sintering rate and sintering temperature rise, an increase in height was still evident at about 3%. Therefore the sintering temperature of between 885°C and 940°C causes an expansion due to the hydrogen that has decomposed from the TiH_2 (particles size of 500 μm). However, when the temperature exceeded 1000°C and above, the shrinkage of height was about 4%. The main cause of this shrinkage could be attributed to the fact that TiH_2 works more effective in molten metal as reported by the Kennedy at al[123]. During heating or heat treatment process an oxide layer forms on the surface of the hydride and the slower diffusion of hydrogen through this oxide is thought to retard the hydrogen release[121]. If within the molten metal, the layer of oxide could be easily broken down and therefore allow the release of the hydrogen atoms.

However, for this sintering process the transient liquid phase sintering creates a small amount of liquid, which will not result into such a stoichiometric reaction from taking place. Therefore, when other samples were sintered at higher temperatures, the shrinkage was much more evidenced. There was little liquid phase formed which generated small pores during sintering thus the hydrogen was released from the TiH_2 in this case.

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Unlike Kennedy et al[122, 124] work on foaming and the creation of large pores. Kennedy et al work's involved in heating the specimens to molten forms and the TiH_2 to react and foam expanding it 200 to 300 times. Indirectly, when the molten stage of the specimens were reached and inevitably intermetallics will be formed. This of course was the opposite to desired goals of the project. At the same time the decomposition of the TiH_2 will assist in pores formation.

Figure 118 Percentage of Height Shrinkage with 40% of TiH_2 (500 μ m) at 20°C/min sintering rate

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Figure 119 Percentage of Height Shrinkage with 80% of TiH₂ (500μm) at 20°C/min sintering rate

Figure 120 Percentage of Height Shrinkage with 40% of TiH₂ (500μm) at 30°C/min sintering rate

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Figure 121 Percentage of Height Shrinkage with 80% of TiH₂ (500μm) at 30°C/min sintering rate

5.6 Porosity Measurement

Several porosity-measuring methods are discussed in this section with the restrictions and limitations highlighted for each method.

5.6.1 Density measurement

The mass of the sample can be found using a set of precision balances while the real volume can be determined by the displacement of a liquid with known density. However, for an accurate volume density, it is important that the pores are interconnected and are exposed at the surface. This method is unable to yield information on average pore size or their distribution.

5.6.2 X-ray radiography and radioscopy

The main limitation of this technique for this specific application is that only a 2-D map of the porous material is obtained. The thickness of the slices is also an important factor;

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if the pore diameter is larger than the thickness then pore identification is difficult. Ideally, the pore diameter should fall within the slice thickness to obtain a true morphology.

Although the high penetration energy of the X-ray results in identification of most pores, if the pores are too many and/or too small then superimposing can be an issue. A limitation of 2-D scanning is that three-dimensional structural features such as pore interconnectivity are not easily obtained and can only be constructed from taking several scans a time consuming process.

5.6.3 X-ray Tomography

The working principal of the X-ray tomograph is that a series of X-ray images of a sample are taken from a large number of directions, usually by rotating and translating the source and the detector around the sample. From the various images obtained the attenuation of the rays at any point of the can be determined and from this local density can be reconstructed mathematically.

X-ray tomography is a relatively expensive instrument equipped with a state of-the-art program to reconstruct the scanned images of the sample. A 3D reconstruction of the images takes a significant amount of time to create. Calibration is necessary before scanning each sample and equipment and software familiarization requires comprehensive training.

The software can generate a 3-D model of the sample showing the internal mapping such as, in the case of sintered material, the pore interconnectivity as well as closed individual pores. Quantitatively, it is capable of calculating the degree of porosity and average pore size.

5.6.4 Eddy-current sensing

The employment of this method requires the passing of a current through the specimen and using the deflection of the secondary coil to map out the porosity. Before the current

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is passed through the specimen a complex calibration procedure has to be undertaken which is specific to the sample's shape and size as well as material composition.

Due to the lack of flexibility, the use of this technique is generally restricted to a small range of applications. The information obtained is only in two-dimensions and therefore a number of scans would be required before a three-dimensional image could be constructed.

5.6.5 Acoustic measurement

The principle of this instrument is that sound waves are used to penetrate into the sample. For the feedback to be determined a certain degree of pore interconnectivity is required. Scanning on dense samples or samples with closed pores will yield little or no results. Furthermore, for greater accuracy it is recommended that at least two scans are taken on each sample.

5.6.6 Porosimetry and permeametry

For porosimetry to be used, the sample requires open pores to be present on the surface to allow the penetration of the gas and mercury into the sample. The technique can be used for the measurement of the pore size, interconnectivity level and volume and distribution of the pores. However, the average pore size cannot be determined with this method.

With all the discussion of the measurement methods a typical analysis result of the image analysis of the porosity as showed in Figure 122 with porosity level of 53.7%.

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Figure 122 Measurement of porosity level of 53.7%

The rest of the results for porosity measurement could be found in the appendix.

5.7 Mechanical Testing with Compression Test

Sintered samples are subjected to mechanical testing such as for example compression testing. The mechanical properties of the parts are important so as to determine the strength and weakness of the materials. The compression testing calculated will give an idea of the Young's modulus of the material. In most biomaterials, the moduli of the materials are too high which causes the migration of bone away from the place where the material was inserted into the subject (i.e human or animal). Ultimately it will cause the loosening of the material within the body and indirectly arise to more mental and physical trauma to the patients.

The samples were prepared and sintered in the Oxy-gon furnace. Flushed with argon gas of 99.99% purity. Two sintering rates and different compositions of the mixes of Ti-Si-Zr of TiH_2 by weight were sintered. Sintering temperatures were set at 885, 940, 1000 and 1050°C.

The machine used was an Instron Model 5569 and the compressive load cell used was 50kN. Compression rate used was 2.54mm/min according to ASTM standard for titanium alloys[62].

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There is a spread of the Young's modulus measurement after the compressive test was carried out. These data collected at each temperature of 885, 940, 1000 and 1050°C was plotted. Four samples were compressed at each temperature and the average of the Young's modulus for each temperature was plotted. There was a decrease in the Young's modulus with the increase of the sintering temperature. At the same time, the porosity was measured by an image analysis program. Four different locations were analysed at the same magnification and the average porosity value calculated.

5.7.1 Heating rate 20°C/min (43µm)

At sintering temperatures of 885 and 940°C the Young's modulus of the samples reached up to about 5.3GPa. This was due to the decomposition of the TiH_2 into titanium and hydrogen. The decomposition temperature for TiH_2 is at about 638°C as reported by Han et. al [121] which falls within our DTA results plotted on Figure 66. This decomposition caused the contraction of samples both in height and diameter (see Figure 106 to Figure 113). The decomposition (stoichiometry of the hydride to $\delta\text{-TiH}_{1.5}$)[123] did not cause the foaming process as there was not enough melts or the temperature was simply just not high enough to turn the samples to molten state. In order for the foaming process to be more effective the metal has to be in molten form[123]. Therefore, this retarded the decomposition kinetics of TiH_2 . However the temperature was high enough to decompose the TiH_2 leaving behind titanium only. At the same time, melting of the mechanically alloyed Ti-Si due to its increase in energy induced onto the powder and increase surface area. The melting of the Ti-Si would allow inter-diffuse between the pure Ti and MA Ti-Si, forming intermetallics, and the samples were left with little porosity formed by the addition of TiH_2 (see Figure 79). This was the cause of such a high Young's modulus at the 885 and 940°C sintering temperature. Taylor et al.[125] and Schuh et. al[126] produced similar levels of porosity of between 5 to 20% at comparable sintering temperature.

The Young's modulus dropped to about 3GPa at about 1050°C with an average porosity increase to 30.91% (see Figure 123) measured. For initial compression of porous material they exhibit initial deformation, a plateau region corresponding to the collapse of the pores and an inflection upward corresponding to densification. Therefore with the difference in Young modulus with varying porosity and a pore structure that would

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elongate in the loading direction (samples at 1050°C) should collapse easily. However samples sintered at 885 and 940°C formed much less pores and more intermetallic (due to melting of the Ti-Si MA powders) contributing to the resistance to deformation compression, which yields a higher Young's modulus. Samples sintered at 1000 and 1050°C have more pores and intermetallic leading to less resistance to compression deformation. More pores also lead to elongation of the pores. Consequently, resulting in a low Young's modulus. Similar to the finding with Thelen et. al[57].

Figure 123 Young's modulus vs Porosity formed during sintering of 43% TiH₂ (43µm) with 20°C/min heating rate(See Figure 124 to Figure 127)

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Figure 124 Calculated average porosity level of 3 different area of the samples is 20.333%

Figure 125 Calculated average porosity level of 3 different area of the samples is 25.373%

Figure 126 Calculated average porosity level of 3 different area of the samples is 8.933%

Figure 127 Calculated average porosity level of 3 different area of the samples is 30.905%

With the addition of more TiH_2 of up to about 80% by weight, the pore formation situation was not improved at all. Owing to the low sintering temperature TiH_2 particles were decomposing but the melting was too little to commence the foaming process. Foaming is more efficient with the metal in molten state as mention by Kennedy et. al[123]. The sintering temperature was allowing the release of the hydrogen atom from the hydride but not at a high rate to result in foaming. Leaving behind the newborn titanium to inter-diffuse with the melts of the Ti-Si alloyed powders. This would create intermetallic along with little pores generated. Consequentially leading to the increase of

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the Young's modulus at sintering temperature of 885 and 940°C. This was more evidence with the shrinkage of the height and diameter (see Figure 106 to Figure 113).

At sintering temperature of 1000 and 1050°C, more pores were formed. The increase in pores corresponded to a decrease in Young's modulus (as measured by compressive testing). The pore elongation (with respect to the direction of the loading) lead to the collapsing of the pores and a lowering in Young's modulus.

Figure 128 Young's modulus vs Porosity formed during sintering of 80% TiH₂ (43µm) with 20°C/min heating rate (See Figure 129 to Figure 132)

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Figure 129 Calculated average porosity level of 3 different area of the samples is 16.622%

Figure 130 Calculated average porosity level of 3 different area of the samples is 25.0.85%

Figure 131 Calculated average porosity level of 3 different area of the samples is 28.073%

Figure 132 Calculated average porosity level of 3 different area of the samples is 29.8025%

5.7.2 Heating rate 30°C/min (43μm)

The results shown in Figure 133 and Figure 138 mirror results for the initial sintering temperatures of 885 and 940°C which showed a high Young's modulus. With the sintering temperature not elevated enough to reach the material's molten state so as to permit the release of the hydrogen atom and trigger the stoichiometry event for the hydride[123].

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With the increase of the sintering temperature there was a change in the porosity, which was the formation of more pores. Indirectly activating the drop in the Young's modulus measurement when the samples were subjected to compression testing. The formation of pores was a direct resultant of the TiH_2 releasing the hydrogen atom in a continuous reaction.

Figure 133 Young's modulus vs Porosity formed during sintering of 40% TiH_2 ($43\mu\text{m}$) with $30^\circ\text{C}/\text{min}$ heating rate (see Figure 134 to Figure 137)

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Figure 134 Calculated average porosity level of 3 different area of the samples is 24.313%

Figure 135 Calculated average porosity level of 3 different area of the samples is 25.235%

Figure 136 Calculated average porosity level of 3 different area of the samples is 28.405%

Figure 137 Calculated average porosity level of 3 different area of the samples is 31.258%

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Figure 138 Young's modulus vs Porosity formed during sintering of 80% TiH₂ (43μm) with 30°C/min heating rate (see Figure 139 to Figure 142)

Figure 139 Calculated average porosity level of 3 different area of the samples is 25.465%

Figure 140 Calculated average porosity level of 3 different area of the samples is 26.605%

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Figure 141 Calculated average porosity level of 3 different area of the samples is 27.232%

Figure 142 Calculated average porosity level of 3 different area of the samples is 30.344%

5.7.3 Heating rate 20°C/min (500μm)

Figure 143 shows the raise in porosity after sintering at 885°C and that at this temperature; the dimensional change is quite unique. This can be explained by using larger TiH_2 particles, which allowed the release larger hydrogen gas while leaving behind relatively large titanium particles. These large Ti particles would give rise to more diffusion of the melted Ti-Si into the 'newborn' Ti. With increased surface and grain boundaries, diffusion is taking place over a larger area. This diffusion between the Ti and the melted Ti-Si created the pores and thus gave rise to the increase in the porosity level (see Figure 94). Oh et. al[57] sintered porous titanium compacts prepared by powder sintering, they used different particles sizes of titanium powder. They were able to produce different porosity levels when sintering with different particle sizes of titanium powders.

The unique expansion of the samples at 885°C was due to the wetting of Ti-Si (see Figure 55 for the liquid formation about 700 to 800°C). This melting of the Ti-Si powder at this temperature was the cause of the expansion of the sample. Researchers like Fujita et. al[97] and Majima et. al[95] working on Ti alloys, witnessed the liquid formation of the aluminium which lead to the expansion of the material during sintering. Their works were in comparison similar to our observed expansion of the samples after sintering at 885°C. The melts of the Ti-Si diffused with the newborn Ti and resulted in the

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intermetallic formation, which explained the higher Young's modulus in this case as the porosity level increased (Figure 143). However at higher sintering rates the porosity increased but the unique expansion of the samples were not observed at all as the sintering increased from temperature of 1000°C to 1050°C. With an increase of the sintering temperature, the porosity level increased as the powder was about to reach it's molten status. This leads to more rapid release of hydrogen atoms from the larger TiH_2 particles. Figure 94 and Figure 97 show the high level of porosity formed, which is relative to the graph plotted in Figure 143.

Figure 143 Young's modulus vs Porosity formed during sintering of 40% TiH_2 (500 μm) with 20°C/min heating rate (see Figure 144 to Figure 147)

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Figure 144 Calculated average porosity level of 3 different area of the samples is 30.519%

Figure 145 Calculated average porosity level of 3 different area of the samples is 44.702%

Figure 146 Calculated average porosity level of 3 different area of the samples is 49.918%

Figure 147 Calculated average porosity level of 3 different area of the samples is 51.014%

In Figure 143 and Figure 148 the yield similar results, at the initial stage sintering temperature at 885°C showed lower porosity level. As the sintering temperature increases the porosity increase and inversely proportional the Young's modulus lowed, computed as compression test were carried out on the sample. The porosity reached a high level of 49-51% at a sintering temperature of 1000 and 1050°C, which will be good promotion of ingrowth bone mention by several researchers[127-129]. The low Young's modulus generated by the porosity will prevent implants from stress shielding that would deteriorate the quality of bone when the Young's modulus for most of the titanium alloys

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were too high[130]. The young's modulus of natural bone was about10-40GPa mentioned by Wen et. al[131]

Figure 148 Young's modulus vs Porosity formed during sintering of 80% TiH₂ (500μm) with 20°C/min heating rate

Figure 149 Calculated average porosity level of 3 different area of the samples is 18.308%

Figure 150 Calculated average porosity level of 3 different area of the samples is 32.912%

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Figure 151 Calculated average porosity level of 3 different area of the samples is 41.435%

Figure 152 Calculated average porosity level of 3 different area of the samples is 53.758%

In general the porosity level generated for the sintering temperatures of 885, 940, 1000 and 1050°C were between 15 to 51% of porosity which was good enough of the ingrowth of bone as mentioned by several researchers like Bobyn et al.[128], Hulbert et al.[127] and Kienapfel et al[132].

The Young's modulus measurement acquired from the compression was good enough to determine the decrease in values with respect to the increase in porosity level. Young's modulus generated from the sintering parameters was within the range of that of natural bone reported by Wen et al.[131] of 10~40GPa.

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5.8 Results with addition of TiH₂

The following section shows the XRD results of the sintered samples at different temperatures (885, 940, 1000 and 1050°C) with varying composition of TiH₂ (e.g. 40% and 80%) and different sintering rates (20 to 30°C/min). Table 14 shows the Gibbs free energy taken from the Thermochemical Data of Pure Substance[133] written by Ihsan Barin. The table shows the different free energy, which will allow the formation of the different phases according to the energy level.

Table 14 Gibb’s Free Energy of the possible formed Phases[133]

Phase formed	ΔH_f (Temperature range 900~1100°C)
TiSi	-129.225~ -129.192 kJ/mol
TiSi ₂	-133.328~ -132.943 kJ/mol
Ti ₅ Si ₃	-577.426~ -577.885 kJ/mol
SiZr	-155.929~ -156.686 kJ/mol
SiZr ₂	-209.505~ -210.671 kJ/mol
Si ₂ Zr	-161.628~ -162.1735 kJ/mol
Si ₃ Zr ₅	-579.614~ -582.875 kJ/mol

5.8.1 Ti-Si-Zr with TiH₂

20°C/min with 43µm TiH₂

The X-ray diffraction (XDR) results displayed a dominant peak of Ti₃Si, which was likely to be formed; as for the composition mix of the Ti-Si was at eutectic point along with sintering temperature of 885 to 1050°C. This phase formation was likely to occur due to fact that the experimental data of de Boer et al.[134] show –53kJ/mol of atom at ΔH°_{298} . With such a low energy required, it was the dominant peak formed. High sintering temperature will attribute formation of any other phases like Ti₅Si₃ and others, which required a higher-level free energy as stated in Table 14. The TiSi phase was not found within the XRD results because the MA powder of Ti-Si had formed a solid solution. Therefore the next possible phase to be formed will be the TiSi₂ phase. This was similar for results of Figure 154 to Figure 156.

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β -Titanium was found in the XRD readings but the intensity of the peaks was lower compared to that shown in Figure 157 to Figure 160. This could be attributed to the difference in the size of TiH_2 particles used. The $43\mu\text{m}$ particle sizes of TiH_2 will decompose to Ti and hydrogen. The Ti will melt easily due to the smaller particle sizes and therefore it will form intermetallic quite easily. There will be β -Titanium formed but at a lower percentage. In Figure 153 to Figure 156 an additional peak of Ti_5Si_4 can be seen which gave the samples a higher compressive strength and indirectly a higher Young's modulus. The small particle sizes of the TiH_2 also attributed to the lower porosity formed. The decrease in porosity level coupled with the intermetallics formed therefore lead to the increase of the Young's modulus

Figure 153 XRD results with 40% $\text{TiH}_2(43\mu\text{m})$ at $20^\circ\text{C}/\text{min}$ sintering rate

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Figure 154 XRD results with 80% TiH₂(43µm) at 20°C/min sintering rate

30°C/min with 43µm TiH₂

This sintering rate was increased from 20°C/min to 30°C/min. Changing the sintering rate was to establish to see if there is a possibility of any phase changes as well as if the porosity will increase. This was undertaken to establish the influence of the sintering rate on phase change formation and porosity. However, from examining the XRD results for both the 40% TiH₂ at 20°C/min and 30°C/min. There was not a great difference in terms of phase changes and porosity level developed during the sintering process, there could have been changes but they were relatively significant as sintering was a temperature driven process. Therefore, with the increase of the sintering temperature new phases will be formed because of this. On the other hand, when comparing the use of the different particle sizes of the TiH₂ employed for the sintering process. There was an extra phase formed by the samples, which used the 43µm TiH₂. The new intermetallic formed was the Ti₅Si₃ phase.

The sintering rate should improve the porosity level generated. However, this was not seen in the samples after the sintering process. This can be attributed to the particle sizes

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of TiH_2 used and the selected sintering temperature. When the sintering temperature starts to melt the TiH_2 powder, a layer of oxide present on TiH_2 will retard the decomposition of the powders to titanium and hydrogen as reported by Kennedy et. al[123]. The presence of this layer will prevent the disassociation of the hydrogen from the titanium. The retarded reaction will foam to form the pores. When the TiH_2 decomposes release the hydrogen atom. The residue will be the titanium due to the small particle sizes the titanium will melt easily which will form the intermetallics with the MA Ti-Si. This was mentioned by German[79] as small particle sizes have more surface area this will accelerate the melting of any powders.

Likewise, with the increase of intermetallics and decrease in porosity formed there was a rise in the Young's modulus in the sintered sample. In Figure 106 to Figure 109 (height) and Figure 110 to Figure 113(diameter) conclusions drawn in the earlier section were found to be similar in this section.

Likewise, the dominant peak formed was Ti_3Si the required free energy level of $-53.0 \Delta\text{H}(\text{kJ/mol.at.})$ was low This was reported by Byun et al.[135] who mechanically alloyed the Ti-Si powders at room temperature. Robins and Jenkins[136] mentioned that the occurrence of silicides increases with increasing atomic weight with Groups IVa and Va. Therefore the Ti and Zr are Group IVb and IIb respectively, the formation of the Ti_3Si and ZrSi_2 were found in the XRD results, which served as a concrete evidence that these two phases are formed during the sintering process.

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Figure 155 XRD results with 40% TiH₂ (43μm) at 30°C/min sintering rate

Figure 156 XRD results with 80% TiH₂ (43μm) at 30°C/min sintering rate

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20°C/min with 500µm TiH₂

The phases formed are as shown in the tabulated results Table 15 with reference to height measured from the XRD results:

Table 15 Measurement of the peaks on the XRD plots

Phase formed	Measurement of the intensity in cm
TiSi ₂	4.5cm
Ti ₃ Si	3.3cm
Zr ₅ Si ₃	1.9cm
SiZr	1.7cm
Ti ₅ Si ₃	1.6cm
Zr ₂ Si	0.9cm
Zr ₅ Si ₄	0.8cm
β-Ti	0.8cm
ZrSi ₂	0.5cm

The main phase formed will be Ti₃Si, which shows the highest intensity and also from the energy required to form at -53.0kJ/mol of atom at ΔH°₂₉₈ by de Boer et al.[134] It required the least energy to be formed when compared to other phases. The TiSi phase was not formed because of the MA powder of Ti-Si, which will be explained later and at the same time Byun et al[135] reported this by experiments that they had carried out for the TiSi phase to form a high energy was required of -64.9 ΔH(kJ/mol.at.) at room temperature. The Ti-Si was mechanically alloyed before hand, consequently, for that phase to form during sintering will be most unlikely. This was evidenced as during the mechanical alloying process, solid solution (where the Si diffused into the Ti lattice) had taken place mention in the earlier section and with traces of iron found. Therefore the TiSi phase was not formed in the sintered samples.

From the XRD analysis, β-Titanium was formed, the promotion of this formation was due to the larger particle sizes of the titanium hydride (TiH₂) employed. The formation of more pores was also found at the same time too when larger particle sizes (i.e 500µm) of TiH₂ was used. Other sintered samples with the same composition but the TiH₂ used were 43µm was size. With the small particle of TiH₂, as the sintering temperature got higher

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the melting of the particles occurred. This allowed the small Ti to melt and diffuse with other melts to form intermetallic. It did have the β -Titanium formed and the porosity formation was lower too. However the β -Titanium formed was higher in intensity in Figure 157. Figure 158 showed a similar intensity of the β -Ti.

From the phase diagram and by knowing the composition and temperature, the Ti_3Si will be the likely phase to be formed. The rest of the intermetallics formed made the sample brittle which in return lower the Young's modulus. The addition of zirconium into the system also lowered the Young's modulus as previously reported by Song et. al[60] who theoretically calculated the mechanical change from the addition of zirconium. As mentioned, in Figure 143 the porosity increased to 51%. The increase in porosity led to a corresponding linear drop in Young's modulus.

Figure 157 XRD results with 40% TiH₂(500µm) at 20°C/min sintering rate

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Figure 158 XRD results with 80% TiH₂(500µm) at 20°C/min sintering rate

30°C/min with 500µm TiH₂

With the increase in the sintering rate, the XRD results showed a clear trend. The domain phase formed was Ti₃Si, which was the highest peak, found in all samples at the different sintering temperatures. The first phase to be formed was Ti₃Si, by the low energy required of -53.0kJ/mol of atom at ΔH°₂₉₈ reported by Schlesinger[137]. Comparing this low level of energy required to form the other phases of required higher energy levels (See Table 14), the Ti₃Si phase will be likely the first phase to be formed. Byun et al[135] reporting on the mechanical alloying of titanium silicides showed similar results of Ti₃Si.

The β-Ti was formed in higher intensity (see Figure 159) compared to other phases found in Figure 153 to Figure 156. This can be attributed to the utilization of the different particle sizes of TiH₂ with 43µm and 500µm. When the sintering temperature increases, the 43µm TiH₂ will release the hydrogen and the Titanium will melt easily due to its small particle size and diffuse to form the intermetallics. The bigger particles size of TiH₂ will also melt and hydrogen will be released but the temperature was not high enough to melt all the titanium in this case.

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The Young's modulus was lower compared to other samples as there were more intermetallics formed in XRD results of Figure 153 to Figure 156. This resulted in samples which had higher Young's moduli as can be seen in Figure 143 and Figure 148, where an elevation in porosity resulted in a decrease in Young's modulus. At the same time the addition of the zirconium into the system lowered the Young's modulus too. This was supported by mathematical modelling undertaken by Song et. al [60].

Figure 159 XRD results with 40% TiH₂(500µm) at 30°C/min sintering rate

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Figure 160 XRD results with 80% TiH₂(500μm) at 30°C/min sintering rate

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6 Conclusion and Future work

In this thesis, a number of metallurgical and manufacturing issues have been introduced and reviewed. The following will summarize the research work and propose future work that can be carried out.

6.1 Conclusions

The application of the Transient Phase Liquid Sintering (TPLS) resulted in the increase of porosity, for Ti-Si-Zr material. Further addition of TiH_2 led to an increase of porosity up to 53.8%. This is in good agreement with German[79] who predicted that when the sintering temperature at is 1050°C undertaken, the formation of a small amount of liquid (melting mechanical alloyed powders), quick rearrangement such as grain boundaries and surface diffusion occurring with little or no intermetallics formed.

Particle size of mechanically alloyed Ni-Ti and Ti-Si decreased with increasing milling time. The reason being that after a prolonged milling time the particles of the Ni-Ti and Ti-Si were broken down to smaller particles. However excessive milling lead to contamination issues. The contamination level became detected after 75hrs for Ni-Ti and 60hrs for Ti-Si.

The effect of applied pressure on the green compact could be clearly observed with higher porosity generated at lower tonnage (30.34% at 0.7023MPa (one tonnage) to 5.63% of 7.023MPa(10 tonnage)).

Results from the investigation on the influence of liquid formation with respect to temperature show excessive liquid formation observed at 1500°C for Ti-Si-Zr as compared to 1050°C .

The lattice parameter ratio c/a and the unit cell volume of h.c.p. Ti were found to decrease with increasing milling time, indicating the shrinkage of Ti lattice due to the diffusion of Si atoms into Ti.

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Initial compaction of the mixed Ti6Al4V powder was pressed with 0.7023MPa and sintered at 950°C above β -transus temperature. It was then cooled down to room temperature within 3hrs before being heated up to 1100°C and subsequently cooled to room temperature (these sintering parameters). The slow cooling coupled with the presence of the vanadium, $\alpha+\beta$ Ti was formed at these sintering parameters.

The sintering of Ti6Al4V at 950°C (with the above mentioned conditions) also created a porous material with porosity at 61.2%.

Samples that utilized TiH₂ to create the pores had more pores formed than samples without the hydride based on the results from the micro tomograph (micro CT).

Sintering temperature at 1050°C with 40 % wt of TiH₂ and a heating rate of 20°C/min were found to be suitable for the formation of a small amount of liquid. The sintering rate had created the right amount of liquid for pores formation and this was verified by the results of the micro tomograph.

Results from the experiments carried out (Section 5.6.2 and 5.6.3) of the mechanical testing, with decreasing the TiH₂ particle size would make the pores become smaller and less well distributed leading to the increase of the Young's modulus.

A smaller TiH₂ particle size led to a greater occurrence of intermetallics at temperatures greater than 1050°C. Below this temperature no intermetallics were detected.

Young's modulus of the samples decreases with the increase in porosity. The melting of the mechanical alloyed powder of Ti-Si will induce a small amount of liquid, causing the occurrence of grain boundaries and surface diffusion which will minimize the formation of intermetallics and retaining the elemental powders. These occurrences will create the pores at the same time during the diffusion. Bigger size particles of TiH₂ are used which result in the creation of more porosity.

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6.2 Future Work

While the Young's modulus for the sintered components approached that of bone, further work could be undertaken to optimise both the mechanical and metallurgical properties of Ti6Al4V and Ti-Si-Zr.

The creation of larger pores (approximately 200 to 500 μ m) would be a desirable goal. Current research work has achieved a rough pore size of 100 μ m and a higher degree of porosity could be achieved with the help of spacers such as carbamides(urea) or ammonium hydrogen carbonate for both of the Ti6Al4V and Ti-Si-Zr material.

Improved mechanical properties and formability could be obtained through the formation of $\alpha+\beta$ titanium. The temperature driven sintering process can be used to achieve this. Increasing the strength of the formed material could allow the material to be used for other implant applications, for example for a hip joint or knee replacement implants.

Self-propagating High temperature Synthesis (SHS) is another manufacturing method which could be used instead of traditional sintering for the Ti-Si-Zr material. The time required in forming the material by SHS is only couple of minutes compared to traditional sintering techniques, which take significantly longer (8 to 10hrs).

To determine the perceived biological benefits of the interconnected pores, cell culturing could be undertaken. In addition, toxicity could be assessed to determine whether ion leaching occurs.

Taking the result generated from this research work, it will be useful to test on living animals to determine the acceptance with regards to osseointegration and bone growth. This will allow the development of spinal implants with possible clinical trials on the pig model first.

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8 Appendix

Figure 161 Isothermal section of Ti-Zr-Si ternary diagram[120]

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Ti-75.50 Al-22.55 V-1.95

Ti-71.90 Al-25.88 V-2.23

Page 134 Point 1 Ti 40.35 Si 1.95 Zr 57.69

Point 2 Ti 94.41 Si 5.14 Zr 0.40

Point 3 Ti 99.88 Zr 0.12

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Page 135 Point 1 Ti 30.61 Zr 69.39

Point 2 Ti 93.96 Si 5.27 Zr 0.77

Point 3 Ti 98.27 Zr 1.73

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Page 136 Point 1 Ti 34.81 Zr 65.19

Point 2 Ti 86.25 Si 11.38 Zr 2.35 Fe 0.03

Point 3 Ti 99.01 Si 0.31 Zr 0.67

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Page 137 Point 1 Ti 47.84 Zr 52.16

Point 2 Ti 85.25 Si 14.38 Zr 0.35 Fe 0.03

Point 3 Ti 99.33 Zr 0.67

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Page 142 Point 1 Ti 71.63 Si 1.29 Zr 27.08

Point 2 Ti 93.82 Si 6.18 Zr 0.10

Point 3 Ti 97.49 Zr 2.51

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Page 143 Point 1 Ti 50.85 Si 9.28 Zr 39.86

Point 2 Ti 92.36 Si 7.08 Zr 0.56

Point 3 Ti 98.64 Zr 1.36

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Page145 Point 1 Ti 82.35 Si 5.29 Zr 12.36

Point 2 Ti 93.82 Si 0.99 Zr 5.19

Point 3 Ti 97.63 Si 0.67 Zr 1.70

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Page 146 Point 1 Ti 67.18 Si 12.96 Zr 15.74 Fe 4.12

Point 2 Ti 92.39 Si 0.62 Zr 6.99

Point 3 Ti 98.01 Zr 1.99

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Page 147 Point 1 Ti 39.74 Si 27.51Zr 32.75

Point 2 Ti 50.61 Si 21.21 Zr 28.18

Point 3 Ti 97.52 Zr 2.48

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Page 148 Point 1 Ti 89.18 Si 8.43 Zr 0.99 Fe 1.25

Point 2 Ti 80.77 Si 0.43 Zr 18.8

Point 3 Point 3 Ti 99.59 Zr 0.41