

**SCHOOL OF MATERIALS AND MINERAL RESOURCES
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**FROM NATURAL BIO-RESOURCE WASTE TO AKERMANITE
BIOCERAMICS FOR SYNTHETIC BONE SUBSTITUTION**

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “**From Natural Bio-Resource Waste to Akermanite Bioceramics for Synthetic Bone Substitution**”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF ABBREVIATIONS

HA	Hydroxyapatite
ICCD	International Centre for Diffraction Data
SEM	Scanning Electron Microscope
TCP	Tri-calcium Phosphate
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

LIST OF SYMBOLS

$\%ts$	Percentage Shrinkage
A	Cross Sectional Area
BD	Bulk Density
CS	Compressive Strength
D	Dry Weight
d	Interplanar Distance
MPa	Megapascal
n	Positive Integer
P	Compressive Load
S	Suspended Weight
t_f	Thickness After Sintering
t_o	Thickness Before Sintering
W	Soaked Weight
$wt\%$	Weight Percent
θ	Scattering Angle
λ	Wavelength Of The Incident Wave
$^{\circ}$	Degree
μm	Micronmeter

SISA PEMBUANGAN SUMBER BIO SEMULAJADI KE SERAMIK AKERMANITE UNTUK PENGANTIAN TULANG SINTETIK

ABSTRAK

Akermanite adalah bio-seramik yang mengandungi Si, Ca dan Mg telah menunjukkan sifat bioaktif dalam keadaan in vivo dan in vitro. Selain itu, ia juga mempunyai ciri-ciri mekanikal dan kadar degradasi yang baik. Dalam kajian ini, pembentukan akermanite dengan menggunakan sisa sumber bio semulajadi telah dikaji. Bahan mentah termasuk kulit kerang, abu sekam padi dan dolomit. Bahan mentah permulaan diolah haba dan ditimbang mengikut formula molekul $\text{Ca}_2\text{MgSiO}_7$. Akermanite telah disediakan dengan menggunakan pengisar bebola kelajuan tinggi, dipeletkan dan disinter pada 3 suhu yang berbeza iaitu 1150 °C, 1200 °C dan 1250 °C selama 3 jam dengan kadar pemanasan 5 °C per minit. Sampel telah dicirikan dengan mengguna XRD, SEM, pengukuran kepadatan, pengukuran ketumpatan. Ujian tegangan lintang juga dijalankan pada sampel disinter. Hasil XRD menunjukkan bahawa hanya puncak akermanite yang ditemui manakala keputusan SEM menunjukkan bahawa jumlah keliangan berkurangan dan saiz butiran bertambah apabila suhu pensinteran meningkat. Ketumpatan dan peratus pengecutan meningkat dengan peningkatan suhu sinter. Kekuatan mampat bertambah apabila suhu sintering meningkat. Di antara semua sampel, sampel akermanite yang disinter pada 1250 °C menunjukkan kekuatan mampatan yang paling tinggi.

FROM NATURAL BIO-RESOURCE WASTE TO AKERMANITE BIOCERAMICS FOR SYNTHETIC BONE SUBSTITUTION

ABSTRACT

Akermanite is a Si, Ca and Mg contained bio-ceramics that shows bioactive properties in vivo and in vitro conditions. Besides, it also has good controllable mechanical properties and degradation rate. In this study, the formation of akermanite by using natural bio-resource waste is studied. The raw materials include cockle shell, rice husk ash and dolomite. The starting raw materials were heat treated and then weighed according to the molecular formula $\text{Ca}_2\text{MgSiO}_7$. The akermanite was prepared using high energy planetary ball mill, palletized and sintered at 3 different temperature which were 1150°C, 1200°C and 1250°C for 3 hours with heating rate 5°C per minute. Characterizations of samples were carried out by using XRD, SEM, density measurement, shrinkage measurement. Diametral tensile strength test was also performed on the sintered samples. XRD results showed that only akermanite peaks were identify whereas SEM results showed that the amount of porosity decreases and the grain size increases when sintering temperature increases. The density and shrinkage percentage increases with the increase in sintering temperature. The compressive strength increased when the sintering temperature increases. Among all samples, akermanite samples that was sintered in 1250°C showed remarkable compressive strength.

CHAPTER 1

INTRODUCTION

1.1 Background

Akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), a Si, Ca and Mg contained ceramic has shown bio-active properties in both in vivo and in vitro conditions (Huang *et al*, 2009). Due to good controllable mechanical properties (Mihailova *et al*, 2015) and degradation rate (Xia *et al*, 2016), akermanite is considered as an interesting material. The raw materials used to form akermanite are limestone, silica and other calcium carbonate source (Huang *et al*, 2009).

There are also reports that eggshell is used as calcium source in producing bio-ceramics. Choudhary *et al*, 2015 used eggshell in a sol gel process to obtain akermanite powder. Wollastonite was also synthesized through microwave (Vichaphund *et al*, 2011) while sol gel methods (Anjaneyulu and Sasikumar, 2014) with the use of eggshell as calcium source. Hence, the results from the researchers shows that eggshell could be a suitable alternative for calcium carbonate for synthesizing the prominent bio-ceramics.

Besides using eggshell as calcium source, cockle shell is also an alternative source of calcium carbonate. The chemical property analysis using X-ray fluorescence (XRF) shows that cockle shell is made up of 97% calcium element and CaO is produced after decomposition was done (Mohamed *et al*, 2012)

Mechanical milling has been reported as one of the most important methods for synthesizing nano powders in bio-ceramics synthesis routes. However, the use of mechanical milling in synthesizing bio-ceramics is very limited as sol gel methods have been utilized. Since the objective of this project is to synthesize akermanite via

economical routes, high speed mechanical milling using planetary mill is chosen as the method for preparation of akermanite bio-ceramics. The use of high energy ball milling as processing technique and bio-natural resources like cockle shell, rice husk and dolomite as starting raw material ensures a low cost and novel synthesis. Mechanical properties of akermanite bio-ceramics produced were assessed in this work.

1.2 Problem Statement

In Malaysia, cockle shell is treated as by products with unpleasant smell and regarded as waste which are typically left at dumpsite to naturally deteriorate (Zulkifli, 2013). Rice husk is an important agricultural residue. Most of rice husk will burn as fuel to generate energy resulting in the waste product, rice husk ash (Li and Wang, 2008). If these rice husk ash are not utilized, it will result in tremendous waste generation, energy loss and environmental pollution. Therefore, it is very important to find ways to utilize rice husk ash comprehensively (Liu *et al*, 2011). Hence, to utilize the unwanted bio-natural resources, cockle shell is treated as the source of CaCO_3 and rice husk is treated as source of SiO_2 . This project aims to raise awareness of possible ways to generate economic return from waste and utilize natural waste as alternative source for akermanite element.

However, there are a wide range of methods that had been proposed for the synthesis of akermanite. The most common method to produce akermanite is the sol-gel based method (Choudhary *et al*, 2015). However, the raw materials for this method is expensive and the products would contain high amount of carbon content which would inhibit densification during sintering. Furthermore, the process that involve several steps, close monitoring of process is required and very time consuming to produce akermanite (Wu and Chang, 2004). Hence, to synthesize akermanite in economical route, bio-natural waste is treated as the starting raw material for this project. The natural waste source

include cockle shell and rice husk , while dolomite is the natural source used as the raw material to extract magnesia (MgO) and calcium oxide (CaO).

Besides, the studies of density measurement, shrinkage measurement, surface analysis, phase analysis and mechanical properties for akermanite bio-ceramics are also required as it is used for bone substitutional. The mechanical properties must be good enough so that it can be applied for load bearing application.

1.3 Objective

The main objectives of the research are:

- a) Synthesis akermanite using natural bio-resource waste and high speed mechanical milling
- b) To determine the mechanical properties of akermanite

1.4 Scope of Research

In this work, akermanite powder is synthesized using high energy planetary ball mill. Various characterizations include X- ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy-dispersive X-ray Fluorescence (XRF) will be used in this study.

The raw materials are cockle shell as source of CaO, rice husk as source of SiO₂ and dolomite as source of MgO and CaO. These raw materials are heat treated in different temperature to obtained required phases. At the beginning of the study, the heat treated raw powders will be characterized using XRD, SEM and XRF. The heat treated powders are then milled and mixed in the planetary mill for 24 hours. Pellets with diameter of 13mm are then prepared and subsequently sintered. Characterization techniques which include X- ray Diffraction (XRD), Scanning Electron Microscope (SEM), shrinkage test

and density test will be used for the sintered pellets at 1150°C , 1200°C and 1250°C. The compressive strength will be tested on the sintered pellet. Figure 1.1 shows the experimental flow chart to produce akermanite.

1.5 Flow Chart of Overall Process

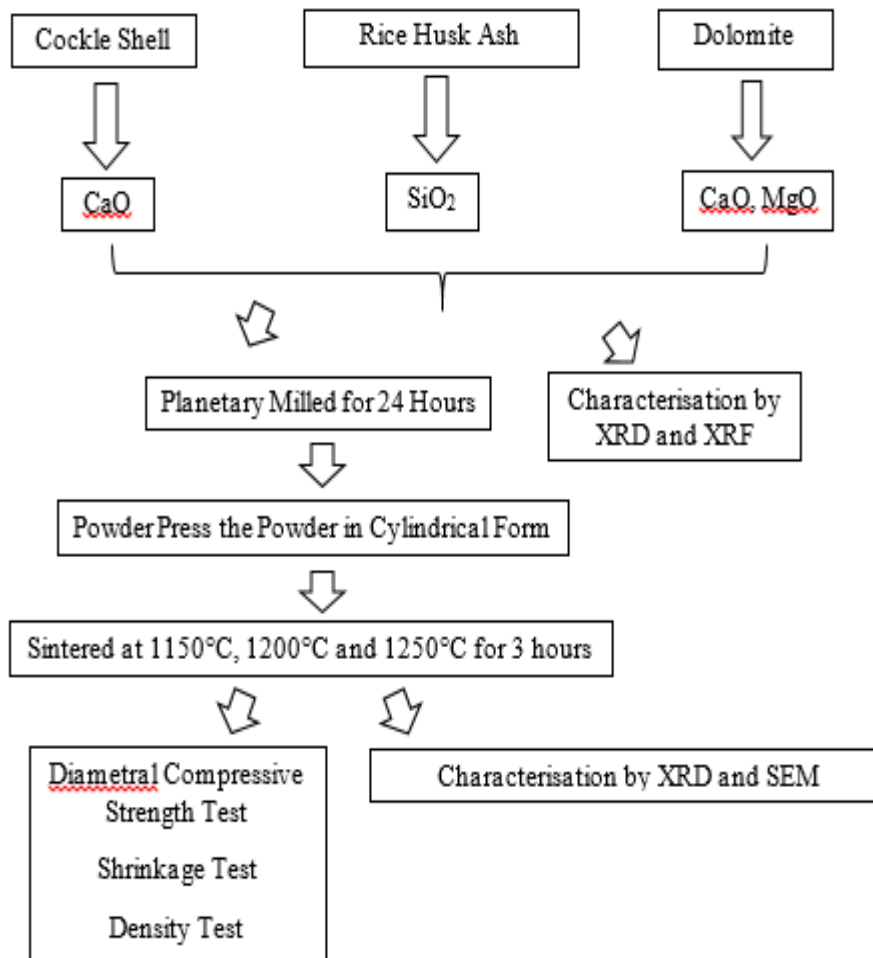


Figure 1.1: Experimental flow chart to produce akermanite from bio-natural resources

CHAPTER 2

LITERATURE REVIEW

2.1 Ceramics

Ceramics are non-metallic in character which distinct from metals and alloys. They have become increasingly inadequate and arbitrary as new ceramics with unusual properties are developed and come into use. (Smallman and Bishop, 1999) Ceramics are manufactured inorganic non-metallic solid materials which have been shaped and fired in a high temperature. The name “ceramic” comes from “keramos”, with the meaning of clay used by potters and object made of clay, which originated from “keramikos” in Greek (The Ceramic Society of Japan, 2012). In its modern context, ceramics contain an extremely broad range of inorganic materials which can be divided into non-metallic and metallic elements. They have wide variety of manufacturing techniques which can be used to produce ceramics. Traditionally, ceramics are moulded from silicate minerals, such as clays, dried and fired at temperatures of 1200-1800°C to give a hard finish. Thus the original Greek word “keramos” represents ‘burned stuff’ or ‘kiln-fired material’ which has long been directly appropriate. However modern ceramics are usually made by the sintering process for example hot pressing, glass devitrification and reaction-sintering (Chaves *et al*, 2017).

Generally, ceramics are classified according to type or function. In industrial terms, they may be listed as pottery, refractories (fire-bricks, silica, alumina, basic, neutral), heavy clay products (bricks, earthenware pipes.), concrete and cement, glasses and vitreous enamels and engineering (technical, fine) ceramics. Engineering ceramics, also known as advanced ceramics, are capable of very high strength and hardness, exceptional chemical stability and can be manufactured to very close dimensional tolerances. Engineering components has been introduced based on considerable scientific

effort and has revolutionized engineering ceramics design practice (Smallman and Bishop, 1999).

In general, the advanced ceramics sector comprises of the following categories (Rödel *et al.*, 2009):

- i. Functional ceramics: Electrical and magnetic ceramics (i.e. dielectrics, piezoelectrics, ferromagnetics), ionic conductors and superconductive ceramics.
- ii. Structural ceramics: Monoliths and composites, for example oxides, nitrides, carbides, borides, and composite materials based on these materials.
- iii. Bio-materials: for example hydroxyapatite and alumina.
- iv. Ceramic coatings: Oxides, nitrides, carbides, borides, cermets and diamond-like coatings, deposited by technologies such as spraying, vapor deposition and sol-gel coating.
- v. Special glasses: Processed flat glass, fire resistant glazing and glasses for optoelectronics.

There have been great interest shown in high technology or advanced ceramic materials among scientists, policymakers and corporations. Varieties of ceramic materials, which hold remarkable properties and able to meet the need for high end applications, have appeared. The substitutions of advanced ceramic materials for traditional parts in many applications result in substantial productivity improvements and high performance (Liang and Dutta, 2001). The development of advanced ceramics has been stimulated by the drive towards higher, more energy-efficient process temperatures and foreseeable shortages of strategic minerals. In contrast to traditional ceramics, advanced ceramics depends upon the availability of purified and synthesized materials and upon close microstructural control during processing (Smallman and Bishop, 1999)

2.2 Bio-ceramics

Bio-ceramics may be defined as engineered materials used specifically for medical applications (Bohner *et al*, 1997). Bio-materials are basically classified into these traditional categories which include bio-metals, bio-ceramics, bio-polymers and bio-composites. Metallic alloys like stainless steel and alloy are mostly applied in orthopedics whereas biopolymers have wide-range of application from linen sutures for closing wounds thousands of years ago until currently modern tissue adhesives and heart valves. However, when it comes to relative biological inertness, ceramics have higher advantage compared with metals making ceramics are more favorable to be used in medicine and dentistry field (Bohner *et al*, 1997).

Bio-ceramics are considered to be materials in oxidized state. By this, an oxidized ceramics will neither degrade in human body nor enter in any biological reactions (Daculsi, 1998). Bio-ceramics have become a diverse class of biomaterials presently including two basic types, i) Bio-inert and ii) Bioactive. Bio-inert ceramics with high hardness are chemically inert whereas bioactive ceramics, during implantation will elicit a host response upon implantation. As bio-ceramic materials are usually used for implantation purposes, the biocompatibility of the materials are important as it will affect the performance of itself. There is a trend that shifted more toward the use of bioactive ceramics, materials that not only elicit normal tissue formation but may also form an intimate bond with bone tissue (Daculsi, 1998).

Bio-ceramic materials have been proven to be an excellent bone substitute in orthopedics and dentistry field due to their resorbability, biocompatibility and osteoconductivity (Bohner *et al*, 1997). There are also several studies that shows that many bio-ceramics could be applied as a delivery system for therapeutic peptides (Ohura

et al, 1996), antibiotics, anti-inflammatory drugs, anti-cancer drugs (Otsuka *et al*, 1994) and bone morphogenetic proteins. The performance of the bio-ceramic materials should be checked for time of periods equaling the life expectancy of the patient as the materials are usually permanently implanted into the living body. However, the interface between host and material cannot be analyzed theoretically as it has to be performed experimentally.

One of the main factors in proliferation and differentiation of various cells is the materials chemistry in the bio-materials (Wu and Chang, 2007). In previous studies, by releasing ions such as silicon, calcium, phosphorus and sodium into the culture medium or body fluid the degradable bio-ceramics may regulate the growth and metabolism of various cells (Xynos *et al*, 2001) and which also activates the expression of related genes to enhance the mineralization and formation of extracellular matrices (Valerio *et al*, 2004).

Bio-ceramics, especially calcium phosphate ceramics have been widely used for bone tissue repair in orthopaedic and dental applications due to their good ability of biocompatibility and osteoconductivity (Xin *et al*, 2005). For decades, materials known as 'bio-active materials' such as sintered hydroxyapatite (HAp) (Hunter *et al*, 1993) and tricalcium phosphate (TCP) (Xin *et al*, 2005) have been synthesized and developed for medical applications. However, there are several drawbacks of these calcium phosphate ceramics in medical applications as they have low bio-resorption rate and poor stimulating effect on growth of new bone tissue. Besides, low crack resistance and small fatigue durability at physiological environment are the major drawbacks for these two materials. These factors restrict them to be used in bulk form of load bearing application such as orthopaedics (Daculsi, 1998). To solve this problem, a new class of bio-active material based on calcium silicate (CaO-SiO₂) with high bio-activity for bone tissue engineering was developed.

Two main characteristics of calcium silicate ceramics compared with calcium phosphate ceramics are excellent bio-activity and bio-degradability. Even so, the main drawback of calcium silicate ceramics and calcium silicate based scaffolds are weak mechanical strength and high degradation which leads to an increased pH value in the environment that is lethal for cells (Iimori *et al*, 2005). Besides, calcium silicate ceramics cannot support human bone cell proliferation (Wu, 2009). Ion modification of calcium silicate ceramics has been utilized to improve their mechanical and bio-medical properties. With Ca-Si-X system (X may be Mg, Zn, Ti and Zr), potential materials have been found for bone tissue regeneration (Wu *et al*, 2005). These material possess good osteoinductivity and osteoconductivity (Heikkila, 2011).

2.3 Requirement for Bio-materials

Bio-materials are predominantly used for replacement for injured or worn body parts. Artificial joints must be completely stable and bio-compatibility as they are installed permanently in human body. The bio-materials must also have high mechanical strength, high fatigue strength and high wear resistance. For the joint parts, they must be able to bear high loads. The survivability of the material is an important aspect to be taken into account as to make sure that the structural requirements being met by the material under consideration. Bio-materials are predominantly used for replacement for injured or worn body parts. This is to ensure the implants that replace body parts can survive for long periods, usually more than 20 years under corrosive and cyclical mechanical loading conditions (Hench, 1991)

2.3.1 Bio-compatibility

Despite satisfying the mechanical requirement for application, a bio-medical ceramics must have a specific set of properties (Hench, 1991):

- Material must be non-toxic
- Device must be stable during implantation
- Material should not corrode or degrade in vivo
- Material should not be carcinogenic

2.3.2 Ceramic Tissue Interaction

In order to achieve attachment towards the musculo-skeletal system, the bio-ceramic must form a stable interface with body tissue. If the body may have to implant material, there will be four response happening (Hench, 1991):

1. Surrounding tissue dies if the material is toxic
2. A coherent interfacial bond will form by the body with the implant if the material is non-toxic and biologically active
3. Tissue will grows to the surface of the material to replace it if the material is non-toxic and easily dissolves.

2.4 Various Compositions of Bio-materials

There are various compositions of bio-ceramics which include (Hench, 2013):

- i. Hydroxyapatite
- ii. Glass Ceramic Tri-calcium Phosphate
- iii. Akermanite

The bio-ceramics are used to product several types of commercial product. Table 2.1 shows the commonly used calcium-based bone substitutes.

Table 2.1: Commonly Used Calcium-Based Bone Substitutes (Pryor *et al*, 2009)

Compound	Sample of Commercial Products
Hydroxyapatite	Pro-Osteon, Bio-Oss, Endobon
Tri-calcium Phosphate	Vitoss
Hydroxyapatite Cements	Bone Source, Mimix Bone Void Filler
Bioactive Glass	Nova-Bone

2.4.1 Hydroxyapatite

Hydroxyapatite, (HA) $[Ca_{10}(PO_4)_6(OH)_2]$ is a calcium phosphate compound that is the primary mineral component of teeth and bone. It is more commonly known as hydroxyapatite cement is made up of calcium phosphate. For the past 30 years, it has been popular in craniofacial and orthognathic surgery, filling bony defects and smoothing contour irregularities. . Hydroxyapatite bio-ceramics was soon developed after bioactive glasses. They could applied as an excellent alternative substrate for bone and tissue regeneration. Besides, they are also excellent bone filler in powder form (Otsuka *et al*, 1990). However, due to its brittleness and relatively low strength, the use of hydroxyapatite for load bearing implant applications such as total hip prostheses and dental implants is not feasible. Hydroxyapatite is frequently used as coating on orthopaedic and dental implants to promote bone ingrowth (LeGeros, 2002). Figure 2.1 shows how hydroxyapatite acts as bone filler to fill the voids or holes formed on the fractured bone

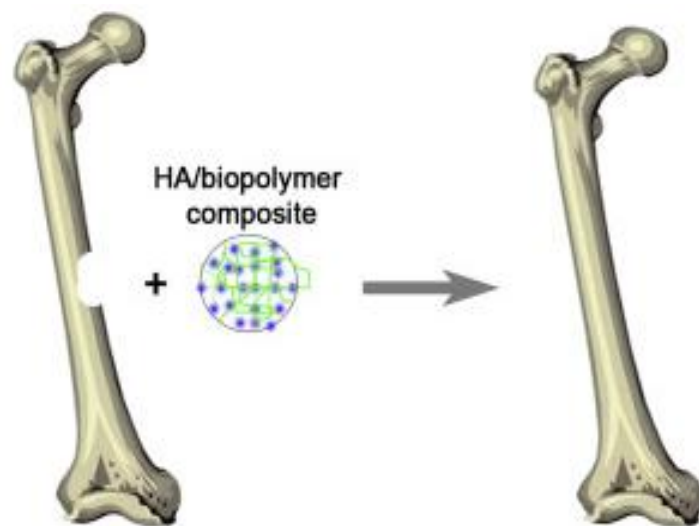


Figure 2.1: Hydroxyapatite as bone filler to fill the voids or holes formed on the fractured bone (Szcześ, 2017)

2.4.2 Tri-calcium Phosphate Ceramics

Tri-calcium phosphate is a tertiary calcium phosphate also known as bone ash [$\text{Ca}_3(\text{PO}_4)_2$] (Ng *et al*, 2005). It serves as a rich source for calcium and phosphorus, which can be easily assimilated and absorbed (Tan *et al*, 2005). Whereas Beta tri-calcium phosphate is highly bio-compatible and able to create a resorbable interlocking network within the defect site to promote healing (Ng *et al*, 2005). Tri-calcium phosphate ceramics are subclass of calcium phosphate ceramics. They have been used widely due to their extremely good natured bio-compatibility characteristics. This is because tri-calcium phosphate has the similar composition of the biological apatite and their ability to form strong bond with the bones. Besides, they are capable of being resorbable (Chae *et al*, 1988). However, there are several drawbacks for tri-calcium phosphate. It has low compressive strength and low fracture toughness in mechanical properties (Miranda *et al*, 2008) and high resorption rate (Boule *et al*, 2000). These reasons have restricted its wider application to bone tissue repair. Figure 2.2 shows regenerated bone support for dental implants using calcium phosphate

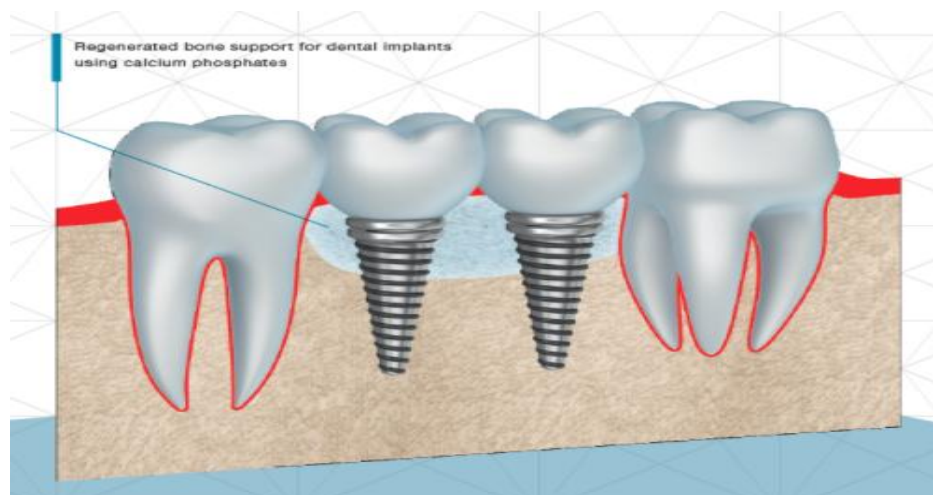


Figure 2.2: Regenerated bone support for dental implants using calcium phosphate

(Bohner, 2000)

2.4.3 Akermanite

Akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) is a Ca, Mg and Si contained bio-ceramics with the melting temperature of 1450°C and density of 2.944g/cm^3 (Wu and Chang, 2006). The three elements in akermanite will give contribution to the human bones and body.

Magnesium (Mg) is an important trace element in the human body which includes bones and extracellular matrix that is closely related to cell differentiation, mineralization of calcined tissue and has an indirect effect on mineral metabolism (Okuma, 2001). Besides, it also can enhance osteoblast adhesion and directly stimulate osteoblast proliferation (Okuma, 2001). Magnesium deficiency in body inhibits cellular growth and increase the risk of osteoporosis (Wolf and Cittadini, 1999).

Whereas for silicon (Si), there are studies that indicate that the mechanism of bioactivity is directly associated with the release of silicon (Wu *et al*, 2005). The amount of silicon doped will affect the properties of the calcium-silicate ceramics. Low concentration of silicon doped will have a stimulatory effect on osteoblasts proliferation but if is doped with high concentration of silicon will have an inhibitory effect on cell proliferation (Hench, 1991). Silicon contributes to the growth of bone tissue (Seaborn and Nielson, 1994) and bone mineralization process (Seaborn and Nielson, 2002). Abnormal bone formation is the results of silicon deficiency (Schwarz and Milne, 1972). However, the bioactivity of ceramics *in vitro* and osteoblasts proliferation is enhanced by silicon (Hing *et al*, 2006). Lastly, silicon ionically joins to Ca to improve the stability of materials (Chen *et al*, 1999).

Calcium (Ca) is one of the most common ions found in human body. It is distributed on the bone and extracellular fluids (Maehira *et al*, 2009). The deficiency of calcium can leads to osteoporosis and bone metabolic diseases (Yasui *et al*, 1991). One of the

properties of calcium is that it is able to regulate osteogenesis by establishing interaction between the osteoblasts and calcium sensing receptor (Zayzafoon, 2006).

From previous studies, it shows that some glasses and glass-ceramics containing Si, Ca and Mg were highly bioactive and could be used for bio-medical applications (Nakamura *et al*, 1985). Diopside ($\text{CaMgSi}_2\text{O}_6$), a Si, Ca and Mg containing ceramic has been reported to be bioactive and can closely bond to bone tissue when implanted in rabbits (Nonami *et al*, 1999).

Diopside is a calcium silicate ceramic that has *in vitro* apatite formation ability and forming bond to bone tissue (Nakajima, 1990). Despite that, degradation rate of diopside is relatively low and can bond directly to bone tissue (Nonami and Tsutsumi, 1999). Generally, diopside shows no sign of toxicity and can form a new uniform junction with new bone tissue (De Aza *et al*, 2005). Combination of diopside with fluoroapatite, wollastonite and akermanite can increase the bioactivity. Lastly, diopside is more suitable for bonding between substrate and coating (Salman *et al*, 2009).

As an analog with diopside in component, akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) is also a Si, Ca and Mg containing ceramic. Hence, it is reasonable to assure that akermanite may be a bioactive material. Akermanite has received more attention due to its improved mechanical properties and low degradation rate (Kokubo and Takadama, 1991). In addition, cells such as bone marrow-derived or adipose-derived stem cells and osteoblasts have displayed better activities or proliferation and osteogenesis on akermanite (Wu *et al*, 2006). Akermanite bio-ceramics promote osteogenesis, angiogenesis and suppress osteoclastogenesis for osteoporotic bone regeneration (Huang *et al*, 2009). An ideal biomaterial for osteoporotic bone regeneration should possess the abilities to promote osteogenesis and angiogenesis meanwhile inhibit osteoclastogenesis (Liu *et al*, 2008). In

previous studies, it shows that Ca, Mg and Si containing akermanite could induce osteogenic differentiation of osteoblasts, adipose derived stem cell in vitro, bone marrow stromal cells and enhance bone regeneration in vivo (Sun *et al*, 2006)

2.5 Synthesizing of Akermanite

Sol-gel methods are the most common method to synthesize akermanite (Choudhary *et al*, 2015). However, the starting raw material for the process are costly and the products would contain high carbon content that will restrict the densification of the ceramics during sintering (Wu and Chang, 2004). Besides, close monitoring of the process is needed as the methods involved several steps. Lastly, these methods are very time consuming for preparing akermanite (Wu *et al*, 2006)

To produce akermanite by a more economical way, bio-natural resource wastes are selected for the starting raw material. Those natural wastes include cockle shell where it is a source of calcium carbonate (CaCO_3), rice husk which contain silica (SiO_2) after burnt and seawater or dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$) that is rich with magnesia (MgO) after being extracted. After obtaining the main substance (CaO , MgO and SiO_2) for akermanite, high energy ball milling aided by sintering is used to synthesize akermanite bio-ceramic. The use of ball milling as the process technique and waste bio-natural resource waste ensures a rapid low cost and novel synthesis.

There are several steps involved in synthesizing of akermanite powder:

- I. Mixing and milling of starting materials
- II. Powder pressing
- III. Sintering

2.5.1 Mixing and Milling of Starting Powder

The milling process is a process in the breaking of large agglomerate into smaller particle for further processing. Planetary ball mills are suitable to use for dry, fine and ultra-fine grinding of particles down to the nanometer size range due to the high stress intensities reached from high accelerations (Karagedov and Lyakhov, 2003). As compared to other ball mill types such as mixer mills or stirred media mills, the advantages of using planetary ball mills are the simple set up, the good cleanability and moderate cost of the device (Bruckmann *et al.*, 2008). Due to the construction of complicated movement of the grinding chamber with high centrifugal forces, planetary ball mills are commonly built only on laboratory and pilot scales, which means with jar sizes up to 1 litre. Typical applications of planetary ball mills are material development and liberation of minerals and other materials for analysis. Planetary ball mills become useful tools for mechanochemical approaches due to its highly efficient mixing of materials in the grinding chamber (Suryanarayana, 1999).

Planetary ball mills are used for sample processing, colloidal grinding and material development due to their good reproducibility, safe handling and short processing times. Planetary ball mills are known for more than a hundred years and normally have 2 or 4 pots. The pots are attached to a disk that rotates around a common central axis while the pots are simultaneously rotating around their own axis. The high rotational speed of both pots and disk causes large impact energies of milling balls inside the pots and thus achieves an effective grinding performance (Stolle *et al.*, 2011).

A planetary ball mill set-up with a normal and counterdirection of the pots and the disk is shown in Figure 2.3. The powder charge influences the ball motion inside and the rotation of the pot. The powder particles are trapped between the colliding balls and

make the collision becomes less elastic so that the ball motion is slowed down and the energy dissipation is reduced (Magini, 1992). The motion of the balls affects the number of collisions and the ball velocity and therefore the impact intensity of the balls which contributes to the energy input to the powder charge (Suryanarayana, 2004). The balls show complex behavior in the grinding chamber during processing. The motion pattern varies depending on the operation parameters. It changes from cascading to cataracting up to centrifugation or rolling with increasing filling ratio or increasing revolution speed (Matsuoka *et al.*, 2010).

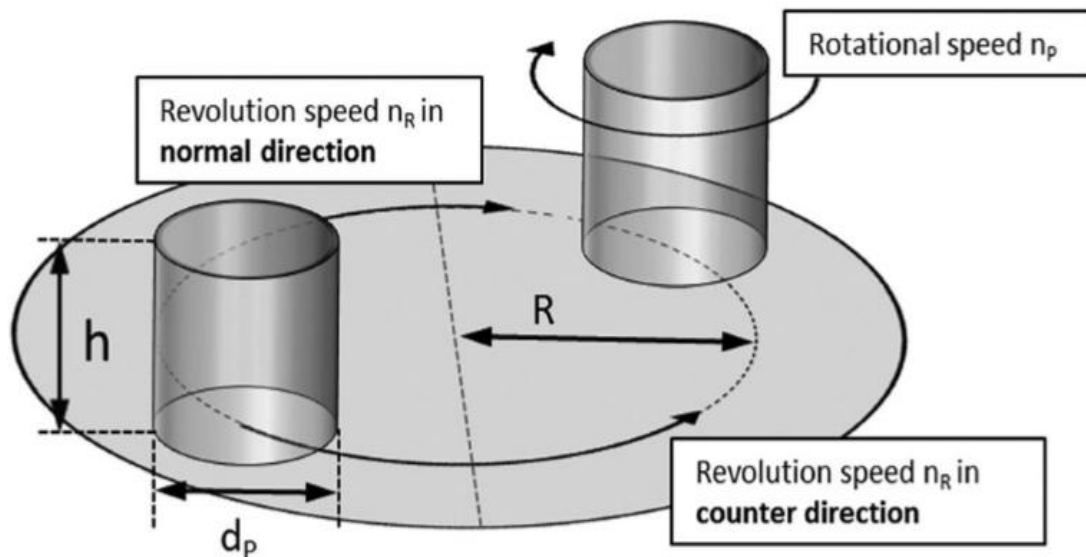


Figure 2.3: Planetary disks with movement in a normal and counter direction, with pot height h , pot diameter d_p , and revolution radius R (Magini, 1992)

As shown in Figure 2.4, in the cascading regime, the milling balls are taken along by the pot wall and unroll upon each other from the bulk top to its base. In the cataracting regime, the balls detach from the wall and impact with high intensity the bulk or the opposite wall. Whereas in rolling or centrifuging regime, the balls align to the wall rotation with almost no relative velocity (Rosenkranz *et al.*, 2011).

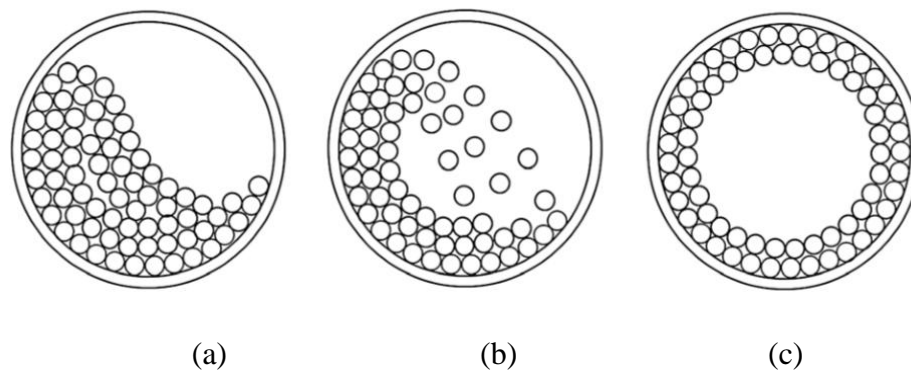


Figure 2.4: Ball motion in a single pot of a planetary ball mill: (a) cascading, (b) cataracting, and (c) rolling (Rosenkranz *et al.*, 2011)

There are a number of variables involving in mechanical milling to achieve different performances (Suryanarayana *et al.*, 2001). The important parameters include type of mill, materials used for the milling vial and balls, ball-to-powder weight ratio, milling speed, milling time, milling environment, temperature controlling and application of electrical or magnetic field during milling. Milling time is dependent on the formation abilities of the designed compounds. A tungsten carbide vial of 250 ml and tungsten carbide balls with various diameters are used as the milling media. Typical ball-to-powder weight ratio is 20:1 and the planetary mill can mill 20 g of powder at a time. The milling temperature is not controlled intentionally. During the milling process, the milling can cause temperature to rise. However, the raised temperatures should be much lower than the calcination temperatures used in the conventional solid-state reaction process (Kong *et al.*, 2008).

2.5.2 Powder Pressing

Powder pressing is a compression of a powder or granules in a rigid matrix (uniaxial pressing) or in a flexible mold (isotactic pressing). Pressing is certainly the most widely used method for shaping ceramic pieces. It allows the making of relatively complex parts with tight dimensional tolerances and high productivity. Uniaxial pressing in a metal mould, with one or two pressing pistons, is used for the production of pieces which thickness is higher than 0.5 mm, with a high surface-to-thickness ratio and exhibiting reliefs only in the pressing direction. On the other hand, isotactic pressing in a flexible mold allows the making of complex shapes with reliefs in three direction and elongated shapes like tubes. Semi-isotactic pressing is the combination of both the metal matrix and a flexible mold (Boch and Niepce, 2010).

Pressing requires a good flow of the powder and a homogeneous filling of the matrix or mould, in order to achieve uniform densities in a reproducible way. Spherical particles with diameter higher than 50 μm exhibit good flow capability. It is therefore necessary to “granulate” ceramic powders in the form of agglomerates, called granules, in order to confer on them the properties required for pressing (Boch and Niepce, 2010).

In uniaxial pressing, the sequence of stages (Figure 2.5) that occur during the pressing of milled powder is as follow (Reed, 1995):

- i. Stage I: rearrangement and stacking of the granules;
- ii. Stage II: deformation or fragmentation of the granules, elimination of porosity between the granules (intergranular macroporosity);
- iii. Stage III: elimination of the microporosity present initially inside the granules (intragranular microporosity), by rearrangement or fragmentation of the particles

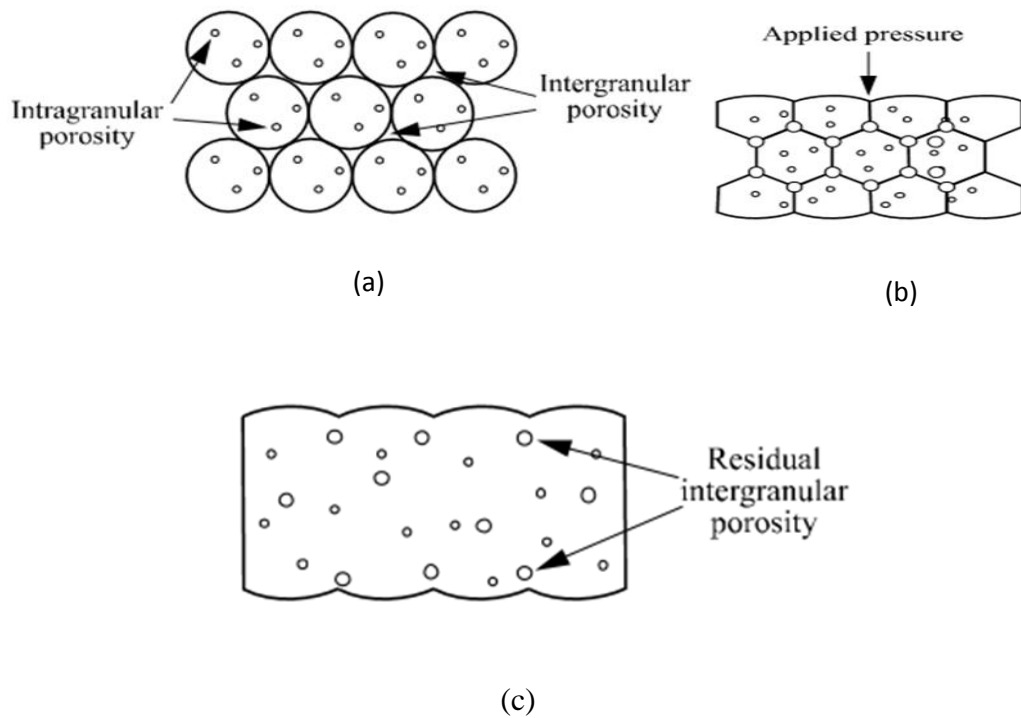


Figure 2.5: Three stages during the pressing of a milled powder: (a) rearrangement of the granules, (b) deformation of granules and (c) removal of intragranular porosity (Reed, 1995)

2.5.3 Sintering

Sintering is one of the oldest processing technologies and but it is by far the most widely used technique for fabrication of many ceramic components (Rahaman, 2007). It is known as an irreversible thermodynamic process in which powder compacts are consolidated using thermal energy to achieve dense and polycrystalline ceramics. The main driving force of sintering is the reduction of the surface free energy of an assembly of particles (Basu and Balani, 2011). This driving force can be increased by reducing the particle size. Besides, the curvature of the particle surface also increases with decreasing

particle size and contributes to the driving force include the application of external pressure or a chemical reaction (De Jonghe and Rahaman, 2003).

The sintering process is interplay between densification and grain growth. It can be divided into three overlapping sintering stages, depending on the changes in the grain size and shape, the pore size and shape, and the related densification kinetics (Malič et al., 2015). The following criteria must be met before sintering can occur (Richerson et al., 2005):

- i. The presence of a mechanism for material transport.
- ii. The presence of a source of energy that activates and sustains this material transport.

The primary mechanisms for transport are diffusion and viscous flow. Heat is the primary source of energy, in conjunction with energy gradients due to particle-particle contact and surface tension. Table 2.2 shows the stages of sintering and its primary physical changes that occur during sintering (Richerson *et al.*, 2005).

Table 2.2: Primary physical changes in each stage of sintering (Richerson *et al.*, 2005)

Stages of sintering	Primary physical changes
1 st stage (Initial)	Rearrangement Neck formation
2 nd stage (Intermediate)	Neck growth Grain growth High shrinkage Pore phase continuous
3 rd stage (Final)	Much grain growth

	Discontinuous pore phase
	Grain boundary pores eliminated

The initial stage involves rearrangement of particles and initial neck formation at the contact point between each particle. The rearrangement consists of slight movement or rotation of adjacent particles to increase the number of points of contact. In addition, bonding occurs at the points of contact where material transport can occur and where surface energy is the highest. The changes that occur during the first stage of sintering are illustrated in Figure 2.6 (Richerson *et al.*, 2005). During the initial stage, the particles become connected with necks, their surface roughness decreases, and a porous network of interconnected particles with a relative density of 60%-70% is formed (Malič *et al.*, 2015).

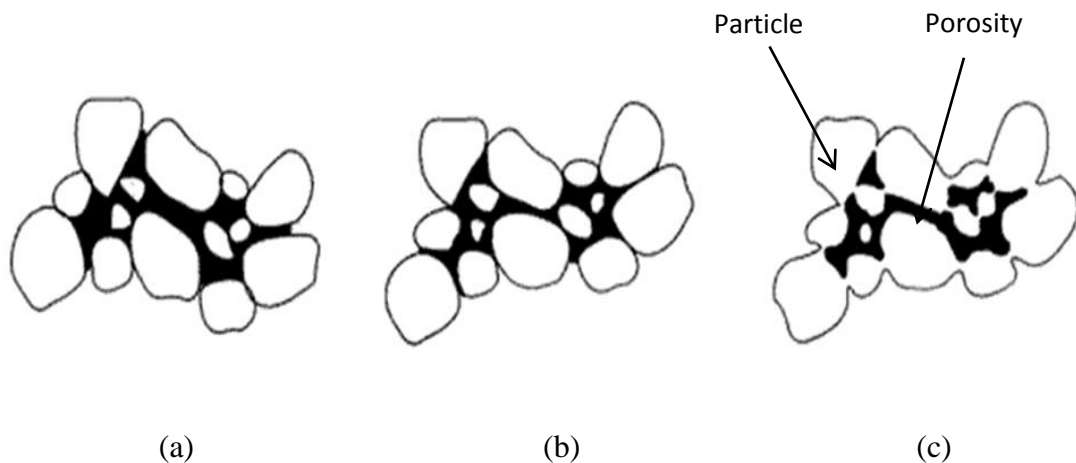


Figure 2.6: Changes that occur during the initial stage of sintering: (a) Starting particles, (b) rearrangement and (c) neck formation (Richerson *et al.*, 2005)

The second stage of sintering is described as intermediate sintering and the physical changes that occur in this stage are illustrated in Figure 2.7. In this stage, porosity decreases and the centers of the original particle move closer together, resulting in shrinkage equivalent to the amount of porosity decrease. The grain boundaries begin to move so that one particle or a grain begins to grow while the adjacent grain is being consumed. The geometry changes as to accommodate further neck growth and removal of porosity (Richerson *et al.*, 2005). This intermediate stage is characterized by rapid shrinkage due to higher densification rate. The pores gradually diminish and the connections between them disappear, resulting in the “closed-porosity” state (usually at a relative density of 92% to 95%).

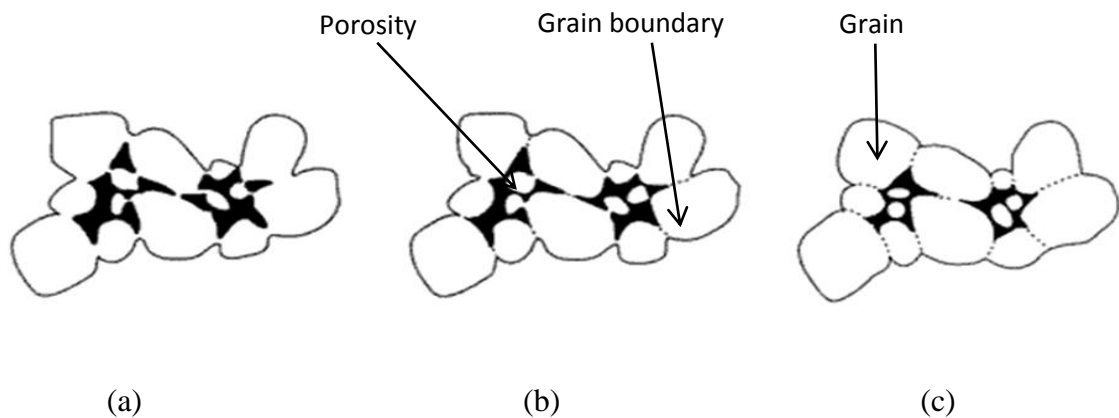


Figure 2.7: Changes that occur during the second stage of sintering. (a) Neck growth and volume shrinkage, (b) lengthening of grain boundaries and (c) continued neck growth and grain boundary lengthening, volume shrinkage, and grain growth (Richerson *et al.*, 2005)

In the final stage, the densification rate gradually decreases, while the isolated pores can either shrink and disappear or merge, and thus grow. The porosity is eliminated by vacancy diffusion along grain boundaries. Therefore, the pores must remain close to