SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA

REFINEMENT OF APATITE CERAMIC PRODUCED FROM WASTE DENTAL MOULD

by

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DECLARATION

I hereby declare that I have conducted, complete the research work and written the dissertation entitled “Refinement of Apatite Ceramic produced from Waste Dental Mould”. 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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TABLE OF CONTENTS

CONTENTS **PAGE**

DECLARATION ii

ACKNOWLEDGEMENTS iii

TABLE OF CONTENT iv

LIST OF TABLES xii

LIST OF FIGURES xiv

LIST OF SYMBOLS xix

ABSTRAK xx

ABSTRACT xxi

CHAPTER 1 INTRODUCTION 1

- 1.1 Background 1
- 1.2 Problem Statement 4
- 1.3 Objectives of Research 5
- 1.4 Research Scope 5

CHAPTER 2 LITERATURE REVIEW 7

- 2.1 Gypsum 7
    - 2.1.1 Application of Gypsum 9
- 2.2 Gypsum Recycling 10
- 2.3 Dental Gypsum 10
- 2.4 Calcium Phosphates Family 11
    - 2.4.1 Hydroxyapatite 14
    - 2.4.2 Tricalcium phosphate 15

2.5 Mechanical Processing and Comminution 17
    2.5.1 Crushing Technique 18
    2.5.1.1 Primary Crusher 18
        2.5.1.1.1 Swing Jaw Crusher 18
    2.5.1.2 Secondary Crusher 19
        2.5.1.2.1 Cone Crusher 19
    2.5.2 Milling Process 20
        2.5.2.1 Planetary Ball Mill 20
        2.5.2.2 Ball Mill 22
2.6 Synthesis Route 23
        2.6.1 Wet Chemical Precipitation Methods 23
2.7 Effect of Reaction Temperature 23
2.8 Effect of pH 24
2.9 Sintering 25
2.10 Biocompatibility of Apatite Ceramics 26
        2.11 Impurities in Apatite Ceramics 27
            2.11.1 Non- hazardous Metal Oxides in Apatite Ceramics 27
            2.11.2 Hazardous Metal Oxides in Apatite Ceramics 28
                2.11.2.1 Chromium 28
2.12 Chromium Removal Methods 29
            2.12.1 Oxidation of Chromium 30
            2.12.2 Chromite Ore Processing Residue (COPR) 30
                2.12.2.1 Caustic Leaching 30
2.13 Characterization of Ground Dental Mould Waste 31
            2.13.1 X-Ray Diffraction Phase Quantitative Analysis 31

for Raw Sample
4.13.2 FTIR Analysis 33
4.13.3 Observation on Particle Shape and Surface Morphology 34
4.13.4 Elemental Analysis of Samples By EDX 36

CHAPTER 3 METHODOLOGY 38

3.1 Introduction 38
3.2 Materials 39
3.3 Work Flow Diagram of Experiment 40
3.3.1 Raw Material Preparation 42
3.3.2 Primary Crushing 42
3.3.3 Secondary Crushing 43
3.3.4 Milling 43
3.4 Raw Material Characterization 44
3.5 Synthesis of Apatite Ceramic Powder from Ground Dental Stone 44
3.5.1 Determination of Calcium-To-Phosphate Ratio 44
3.5.2 Project 1: Synthesis of Hydroxyapatite 45
3.5.3 Preparation of Sodium Hydroxide Solution 45
3.5.4 Precipitation of Calcium Hydroxide 46
3.5.4.1 Project 1st stage: Oxidation of Chromium 47
3.5.4.2 Chromium Extraction by Chromite Ore Process Residue Method (COPR) 47
3.6 Project 1 2nd Stage: Synthesis of Hydroxyapatite 48

3.6.1 Preparation of Calcium Hydroxide Suspension 48
3.6.2 Preparation of Phosphoric Acid Solution 49
3.6.3 Precipitation of Apatite Ceramic 50
3.6.4 Filtering and Washing of Precipitate Collected 50
3.6.5 Drying 51
3.6.6 Grinding of Dried Precipitate from 2nd Stage 51
3.6.7 Pressing Pellets 51
3.6.8 Sintering 52
3.7 Sample Labelling 53
3.8 Heat Treatment on Ground Dental Mould Waste 55
3.9 Simulated Body Fluid Test (SBF) 55
3.10 Diametral Compression Test 59
3.11 Vickers Hardness Test 60
3.12 Characterization Methods 61
3.12.1 X-Ray Diffraction 62
3.12.2 X-Ray Fluorescence 63
3.12.3 Fourier Transform Infrared Spectroscopy 63
3.12.4 Field Emission Scanning Electron Microscopy 64
3.12.5 Energy Dispersive X-ray (EDX) Spectroscopy 65
3.13 Bulk Density and Apparent 65

Porosity Analysis
3.14 Shrinkage Analysis 67

CHAPTER 4 RESULTS AND DISCUSSION 68

4.1 Ground Dental Stone Waste 68
4.1.1.1 Elemental Analysis by X-Ray Fluorescence Spectroscopy 68
4.1.2 Chromium Removal Method 70
4.1.3 Oxidation of Chromium (III) Oxide to Chromate 70
4.1.4 Chromite Ore Processing Residue (COPR) Method 70
4.1.4.1 Alkaline Roasting 71
4.1.4.2 Mass of Roasted Dental Stone Obtained 71
4.1.4.3 Atomic Absorption Spectrometry Analysis for Leached Solution 72
4.1.4.4 Observation on Particle Shape and Surface Morphology 72
4.1.4.5 Elemental Analysis of Leached Residues by EDX 74
4.1.5 Reaction between Ca(OH)2 and Phosphoric Acid 76
4.1.5.1 Colour of Powder Reaction Ca(OH)2 and Phosphoric Acid 76
4.1.5.2 X-Ray Diffraction Phase Quantitative 77

Analysis for Apatite Ceramics
4.1.5.3 FTIR Analysis for Roasted 2nd Stage 79
4.1.5.4 Observation On Particle Shape And Surface Morphology For BHA Sample 81
4.1.5.5 XRF of Apatite Ceramic Powder 83
4.1.6 Sintering Stage of Apatite 84
4.1.6.1 Visual Observation on the Changes in Appearance of Sintered Apatite Pellets 84
4.1.6.2 X-Ray Diffraction Phase Quantitative Analysis for Sintered SHA Pellets 86
4.1.6.3 Observation on Particle Shape and Surface Morphology on SHA Sample 88
4.1.6.4 SBF Test 91
4.1.6.5 Shrinkage Measurement on the Sintered SHA Pellets 92
4.1.6.6 Apparent Porosity and Bulk Density Measurement on the Sintered SHA Pellets 93
4.1.6.7 Compressive Test on the Sintered SHA Pellets 95
4.1.6.8 Vickers Hardness on Sintered SHA Pellets 96
4.2 Heat Treatment for Dental Stone Waste 97
4.2.1 SEM Image for Green Stone Powder 97
4.2.2 SEM Image for Crushed Dental Stone 98

Waste
4.2.3 X-Ray Diffraction Analysis Heat Treated Sample 99
4.2.4 FTIR Analysis between Heat Treatment Samples and Green Stone 104
CHAPTER 5 CONCLUSION AND SUGGESTIONS 105
5.1 Conclusion 105
5.2 Suggestions for Future Work 106
REFERENCES 107

APPENDIX 114

LIST OF TABLES

PAGES

Table 2.1 Different types of calcium phosphate apatite ceramics 12

Table 2.2 Percentage of phase present in each milling technique. 33

Table 2.3 Elements detected in ground dental stone wastes by EDX. 36

Table 3.1 Coding designated for leached residue after leaching process 53

Table 3.2 Coding designated for apatite samples in project 1, 2nd stage before sintered. 53

Table 3.3 Coding designated for samples in sintering stage. 54

Table 3.4 Coding designated for samples in Heat Treatment process. 54

Table 3.5 Order, amounts, weighing containers and formula weights of reagents for preparing 1000 ml of SBF 56

Table 4.1 Weight percentage of each element present in each milling technique by XRF. 69

Table 4.2 Average mass of roasted ground dental stone. 71

Table 4.3 Amount of Cr^{6+} of caustic leaching using 7M NaOH. 72

Table 4.4 Amount of each element detected in leached residue by EDX analysis. 75

Table 4.5 Percentage of phase present in roasted synthesized apatite powder of sample BHA 5M and BHA 7M. 79

Table 4.6 Weight percentage of each element present in BHA3M, 83

BHA5M and BHA7M by XRF.

Table 4.7 Percentage of phase present in roasted synthesized apatite powder of sample SHA 3M, SHA 5M and SHA 7M. 88

Table 4.8 Percentage of phase present in heat treatment sample of green stone, HTG-125-2H, HTG-125-4H, HTG-160-2H and HTG-160-4H. 103

LIST OF FIGURES

PAGES

Figure 2.1 a) Crystal lattices of a gypsum, b) hemihydrate and c) anhydrite (Charola et al., 2006). 8

Figure 2.2 Dental stone in powder form (McCabe and Wall, 2008) 11

Figure 2.3 Types of jaw crusher (Gupta and Yan,2006) 17

Figure 2.4 Schematic diagram of planetary ball mill depicting the ball motion inside the milling jar (Suryanarayana, 2004). 21

Figure 2.5 Schematic diagram of planetary ball mill illustrating the Rotation and revolution of pot (Oleg et al., 2009). 21

Figure 2.6 Development of the ceramic microstructure during sintering: (a) loose powder particles, (b) initial stage, (c) intermediate stage and (d) final stage (adapted from Lee and Rainforth, 1994). 25

Figure 2.7 Simplified schematic of industrial production of chromate (modified from Deakin et al.). 30

Figure 2.8 X-ray Diffractrogram of Ground Dental Stone Waste (Ezuddin,2016). 32

Figure 2.9 Fourier transform infrared spectrum for ground dental stone waste (Ezuddin, 2016). 34

Figure 2.10 SEM image of Planetary ball milled at 1000 & 5000 times magnification. 35

Figure 2.11 SEM image of puck & ring milled at 1000 & 5000 times magnification. 35

Figure 3.1 Dental stone waste collected from AMDI. 39

Figure 3.2 Flowchart diagram of experimental work. 41

Figure 3.3 Swing Jar Crusher 42

Figure 3.4 Heating profile for alkaline roasting of ground dental stone. 48

Figure 3.5 Heating profile for sintering of the pressed apatite pellets. 47

Figure 3.6 Arragement of sample in SBF solution (Kokubo and Takadama, 2006). 52

Figure 3.7 Apparatus Setting of Preparation of SBF solution. 52

Figure 3.8 (A) and (B) Apparatus setting of SBF test. 52

Figure 3.9 View of Diametral Compression Test machine. 59

Figure 3.10 The pellet coated by Ag layer. 60

Figure 3.11 The view of Vickers Hardness Test machine. 61

Figure 3.12 Equipment set up for Bulk Density and Apparent Porosity Analysis. 66

Figure 4.1 SEM image of caustic leached residues with 3M NaOH at 1000 & 5000 times magnification. 73

Figure 4.2 SEM image of caustic leached residues with 5M NaOH at 1000 & 5000 times magnification. 73

Figure 4.3 SEM image of caustic leached residues with 7M NaOH at 3000 times magnification. 73

Figure 4.4 Precipitate Obtained In Roasted 2nd Stage. 74

Figure 4.5 Fourier transform infrared spectra for roasted apatite powder synthesized by using 3M, 5M and 7M of sodium hydroxide solution. 77

Figure 4.6 X-ray Diffractrogram of synthesized BHA 5M and 7M 78

Figure 4.7 SEM image of roasted apatite powder synthesized by 3M of NaOH for leaching process with magnification of 10K times (A) and 30K times (B). 80

Figure 4.8 SEM image of roasted apatite powder synthesized by 5M of NaOH for leaching process with magnification of 10K times (A) and 30K times (B). 81

Figure 4.9 SEM image of roasted apatite powder synthesized by 7M of NaOH for leaching process with magnification of 10K times (A) and 30K times (B). 82

Figure 4.10 Sintered apatite materials by 3M NaOH for leaching process. 85

Figure 4.11 Sintered apatite materials by 5M NaOH for leaching process. 85

Figure 4.12 Sintered apatite materials by 7M NaOH for leaching process. 85

Figure 4.13 X-ray Diffractrogram of synthesized SHA 3M, SHA 5M and 7M. 87

Figure 4.14 SEM image of roasted apatite powder synthesized by 89

3M of NaOH for leaching process (SHA 3M) which after sintering with magnification of 3K times.

Figure 4.15 SEM image of roasted apatite powder synthesized by 5M of NaOH for leaching process (SHA 5M) which after sintering with magnification of 3K times. 91

Figure 4.16 SEM image of roasted apatite powder synthesized by 7M of NaOH for leaching process (SHA 7M) which after sintering with magnification of 1K times and 5K times. 92

Figure 4.17 SEM image of SHA 7M sample in 1 Day SBF test with magnification of 1K times and 5K times. 94

Figure 4.18 SEM image of SHA 7M sample in 3 Day SBF test with magnification of 1K times and 5K times. 94

Figure 4.19 SEM image of SHA 7M sample in 7 Day SBF test with magnification of 500 times and 5K times. 95

Figure 4.20 Bar chart showing shrinkages in all SHA samples. 96

Figure 4.21 Bar chart showing Apparent Porosity and Bulk Density in all SHA samples. 97

Figure 4.22 Bar Chart of Compressive Test value for SHA sintered Pellet. 98

Figure 4.23 Bar Chart of Vickers Hardness value for SHA sintered Pellet. 99

Figure 4.24 SEM image for green stone in magnification of 101

3000 times and 5000 times.

Figure 4.25 SEM image for crushed dental stone with magnification 1000 times and 5000 times. 100

Figure 4.26 X-ray Diffractrogram of Green Stone, HTG-125-2H and HTG-125-4H 103

Figure 4.27 X-ray Diffractrogram of Green Stone, HTG-160-2H and HTG-160-4H. 104

Figure 4.28 FTIR of Green Stone, HTG-160-2H and HTG-160-4H. 106

LIST OF SYMBOLS

n_1	Number of mole
M1	Molarity of the solution
V1	Volume
λ	Wavelength
d	Interplanar spacing
θ	Scan angle for XRD
D	Dried weight
W	Saturated weight
S	Suspended weight

APATIT YANG DIHASILKAN DARIPADA BATUAN GIGI

ABSTRAK

Menurut Advanced Medical And Dental Institute USM (AMDI), institut itu membuang 50 kg sisa acuan gigi setiap bulan. Sisa acuan gigi hanya dibuang sebagai sisa perubatan. Bagaimanapun, sisa acuan gigi mempunyai kemungkinan sumber kalsium yang boleh membentuk bahan bioceramics apatite apabila bertindak balas dengan asid fosforik. Biokeramik yang boleh menjadi sintesis dari sisa acuan gigi terutamanya Tricalcium Phosphate (TCP) atau Hydroxyapatite (HA). Dalam kajian ini, ia mempunyai dua projek; Sintesis bioceramics apatite dari sisa acuan gigi dan rawatan haba kepada sisa acuan gigi untuk mengitar semula ia sebagai bahan mentah untuk membuat acuan gigi. Projek sintesis material bioceramics apatite, ia mengguna pakai Residual Pemprosesan Bijih Chromite (COPR), berikut oleh larutan kaustik dengan penyelesaian 3M, 5M dan 7M natrium hidroksida (NaOH). Hasilnya menggunakan 7M NaOH dalam pencucian kaustik dapat menghilangkan kandungan kromium sepenuhnya dari residu tersair dan membentuk warna putih bahan bioceramic apatite apabila bertindak balas dengan asid Phosphoric. Yang utama fasa bahan apatite adalah Tricalcium Phosphate (TCP) selepas disinter pada 1100 ° C. Untuk projek ke-2, sisa acuan gigi menjalani rawatan haba pada 125 ° C dan 160 ° C selama 2 jam atau 4 jam. Produk rawatan haba membentuk fasa utama, iaitu Bassanite, salah satu plaster paris. Oleh itu, keputusan awal menunjukkan ia dapat dikitar semula untuk digunakan sebagai bahan mentah untuk acuan gigi lagi.

REFINEMENT OF APATITE CERAMIC PRODUCED FROM WASTE DENTAL MOULD

ABSTRACT

According to Advanced Medical And Dental Institute USM (AMDI), the institute disposed 50 kg of dental mould waste per month. Dental mould waste was just thrown as medical waste. However, Dental mould waste has possibility of calcium source which can form apatite bioceramics materials when react with phosphoric acid. Bioceramics that can be synthesis from dental mould waste mainly Tricalcium Phosphate (TCP) or Hydroxyapatite (HA). In this study, it has two projects; synthesis apatite bioceramics from dental mould waste and heat treatment to dental mould waste to recycle it as raw material for making dental mould. The project of synthesis apatite bioceramics material, it adopts Chromite Ore Processing Residue (COPR), following by caustic leaching with 3M, 5M and 7M of Sodium Hydroxide (NaOH) solution. The result using 7M NaOH in caustic leaching was able to fully removed chromium content of leached residue and forming white color of apatite bioceramic material when react with Phosphoric acid. The main the phase of apatite material was Tricalcium Phosphate (TCP) after sintered in 1100 °C. For 2nd project, dental mould waste undergone heat treatment at 125 °C and 160 °C for 2 hour or 4 hour. Heat treatment product form main phase, which was Bassanite, one of the plaster of paris. Thus, preliminary result show it can be recycled to use as raw material for dental mould again.

CHAPTER 1

INTRODUCTION

BACKGROUND

Biomaterial is a material which can replace a part or substitute a defect component in human body. The biomaterial should be safe, reliable and physiologically acceptable in the human body. It is mostly used in the treatment of injury caused by trauma and disease. It is a synthetic material used to replace part of body which connects with living tissue. The purpose of using biomaterials is to restore the function of natural living organ and tissue for human health (Park & Lakes, 2007).

The characteristics of biomaterials are biocompatibility with tissue, nontoxic and nonallergenic to human body, chemically stable and inert when place in human body, suitable density and weight, easily available with suitable mechanical strength and longer fatigue life (Park & Lakes, 2007). Generally, the application of biomaterials are in Joint replacements, Bone plates, Bone cement, Artificial ligaments and tendons, Dental implants for tooth fixation, Blood vessel prostheses, Skin repair devices, Cochlear replacements and Contact lenses (Tathe & All, 2010).

Gypsum is one potential source of raw materials for the biomaterials. It is a mineral that is found in earth crust. It can be used as the source of calcium for apatites as Gypsum is composed of calcium sulfate ($CaSO_4$) and water (H_2O), which is Calcium Sulphate Dihydrate ($CaSO_4.2H_2O$). Plaster of Paris is produced from Gypsum and when heated around 160 °C in kiln, it will lose water to form Plaster of Paris. The chemical reaction will undergo like the following (McCabe, 2008):

$$\underset{\text{(Gypsum)}}{CaSO_4.2H_2O} \xrightarrow[\boxed{\text{Heat (160 }^{0}\text{C)}}]{} \underset{\text{(Plaster of Paris)}}{CaSO_4 \bullet \tfrac{1}{2} H_2O} + \underset{\text{(steam)}}{H_2O}$$

When addition of water to Plaster of Paris, it becomes hardened due to water absorption, the rehydration reaction occur like the following, to form a dihydrate:

$$\underset{\text{(Plaster of Paris)}}{2\ CaSO_4 \bullet \tfrac{1}{2} H_2 O} + 3\ H_2O \longrightarrow \underset{\text{(Calcium Sulphate Dihydrate)}}{2CaSO_4 \bullet 2H_2O} + \text{heat}$$

In the case of dental stones, it may be produced from gypsum which is heated around 125°C under steam pressure condition. It will form α-hemihydrate, which produce a less porosity for hemihydrate materials. Most manufacturers will add some chemical component to dental stones which would easily allow people to differentiate that materials as dental stones which is white color (McCabe, 2008).

In this study, it is an attempt to produce apatite from waste dental stone. Apatite could be Hydroxyapatite (HAP) or Tricalcium Phosphate (TCP). Hydroxyapatite, $Ca_{10}(PO_4)_6 (OH)_2$ is a primary mineral content for human body's calcified cartilage and bone

(Ravaglioli, 1992). It has some of desirable physiochemical properties such as inertness for chemical reaction, good biocompatibility and stability to human body, which make it suitable to become biomaterial. In the past, it is used for surgical implantations in medical application. As comparison with calcium phosphates, HAP is very fast for reconstructive-resorption activity for implementation part of bone (Ravaglioli, 1992).

On the other hand, Tricalcium Phosphate (TCP) have 3 polymorphs, which is low-temperature β-TCP, and the high-temperature forms, α- and α'-TCP. However, α'-TCP is hard to exists because it only exist at temperatures more than 1430 ^{0}C and it reverts almost instantaneously to α-TCP on cooling below the transition temperature. β-TCP is stable at room temperature and it will transforms into α-TCP at 1125°C, which is metastable. It will retain this form until room temperature during the cooling although rapid cooling is required. Theoretically, TCP will degrade when new tissue growth and replace it after implantation. Due to this reason, implantation of TCP does not have problem of interfacial stability in human body (Mirhadi et al.,2011)

Recycle is a must in Malaysia because it can reduce the needs of materials to reduce the impact of environment. It promote a "green" consciousness to society every day (Recycling, 2008).

1.2 Problem Statement

Dental mould is a component that dentist use for making the model structures of human teeth for patient with tooth defect. But once patient recover and obtain their dentures, the dental mould are dispose as medical wastes in clinic. If these waste manage are dispose in landfill, the sulphate contain of dental mould could pollute the environment. However, the Environmental Permitting (England and Wales) Regulations 2010 mention it cannot be dump in landfill.

According to the record of Advanced Medical And Dental Institute USM (AMDI), the institute disposed 50 kg of dental mould per month. The interesting part is the waste dental mould is a possible calcium source for forming the apatite materials. The challenge is that the green mould waste contains Chromium which the element has to be removed completely, before forming apatite that would be acceptable as a bioceramic material. Suitable route has to be chosen to ensure complete removed of the chromium. In this study, Chromite Ore Process Route (COPR) mainly roasting of the waste dental mould and leaching with Sodium hydroxide (NaOH) was employed. This was they reacted with phosphoric acid to form apatite ceramics.

Another issue is to investigate if the used waste dental mould would be recycled by heat treatment to convert to form Plaster of Paris hemihydrate. Heat treatment at 125 °C and 160 °C was adapted in this study.

1.3 Objectives of Research

The objectives of this research are listed as below:

- Investigate caustic leaching method with difference concentration of sodium hydroxide (3M, 5M and 7M) to remove chromium content from waste dental stone.

- To study to possibility of synthesising apatite ceramics for the waste dental mould.

- investigate the possibility of dental mould waste to be recycled as raw material for dental mould by heat treatment procedure.

1.4 Research Scope

In this study, the research scopes were focused on synthesis of apatite ceramics from ground waste dental stone and removing the chromium present via caustic leaching method. The dental stone wastes were determined as gypsum, $CaSO_4.2H_2O$ and thus suggests as a potential calcium source.

In general, the process of converting the gypsum to apatite bioceramics are conducted into 4 main sections:

i. Characterization of crush raw dental mould.

ii. Synthesis and characterization of apatite ceramic powders and its sintered product by using Chromite Ore Process Route (COPR).

iii. Characterization of crush raw dental stone after heat treatment procedure.

CHAPTER 2

LITERATURE REVIEW

2.1 Gypsum

Gypsum is a common mineral, found in sedimentary environments. It is naturally found in rock form. Gypsum will turn to anhydrite under high temperature and pressure. In the dawn of record history, it was used as building materials. In ancient time almost 5000 year ago, Pharaohs of Egypt used it as the materials for the construction of their royal tombs. In year 2015, the production of cruel gypsum was estimated at 11.5 million ton, worth around $98 million. In United State of America, manufacturers of wallboard and plaster products consumed approximately 90% of domestic used, in which total gypsum produce from United State of America by approximately 26.8 million tons.

Gypsum is one of the form of Calcium Sulphate. When Calcium Sulphate in contact with water, it will crystallize and form gypsum (dihydrate). The crystal structure of gypsum is monoclinic, being prismatic to acicular shape or elongated tabular shape, it will form rosette-like aggregates according to its shapes. Due to gypsum and its anhydride are rock forming mineral, it is also referred as gyprock. It is commonly deposited in salts pan and saline lake, some of them can be deposited until hundred metre of thickness (Charola et al., 2006).

In late nineteenth century, scientists had investigated the equilibrium between gypsum, anhydrite and hemihydrate. Some scientists like Le (1887) showed about the heating curves of gypsum which corresponded to the subsequent dehydration into the anhydrous phase and partial dehydration into the hemihydrate at 128 and 163 °C with slow reaction. If required fast reaction for dehydration reaction, Heusinger (1906) highlight that it required at least 107 °C for the dehydration reaction. Dehydration rate of gypsum could be determined by its crystallinity and particle size. Hulett and Allen (1902) found that solubility will reach maximum at 40 °C. Gypsum shows a layered structure with the water molecules which alternating with calcium sulphate layers. It shows that gypsum are able to lose its coordinated water without disrupting its crystal lattice structure as Figure 2.1(Charola et al., 2006).

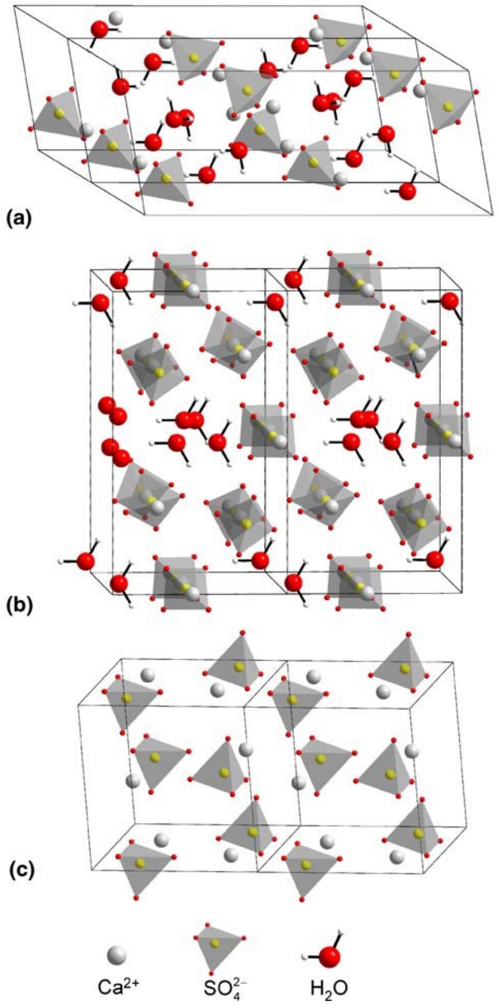

Figure 2.1: a) Crystal lattices of a gypsum, b) hemihydrate and c) anhydrite (Charola et al., 2006).

2.1.1 Application of Gypsum

Mostly gypsum are used in production of gypsum blocks, plasterboards and gypsum fibreboards. Basically, it is applied largely in construction and building product based on its mineral content (purity). For high purity gypsum, it is used in medical application like surgical and dental work, and making plaster moulds in the pottery industry for certain application. Natural gypsum is suitably used in manufacturing of building plaster (Euro Gypsum,2007).

Besides that, gypsum are used in agriculture technology. It being used for agriculture over more than 200 year as fertiliser and soil amendment. Gypsum is able to improve the workability and water penetration of impermeable 'alkali' soils. The clay present inside gypsum are able to soften the soils. At the same time, gypsum can control the pH value of soil and neutralise the acidity of soil. Gypsum contain calcium and sulphur which can be added as nutrient to the plant(Euro Gypsum,2007).

2.2 Gypsum Recycling

Gypsum is a recyclable material. The gypsum waste can be used in aggregates in road construction. The gypsum waste can be ground into powder, then it is re-introduced with controlled blend into the manufacturing process for other application. Nowadays, only small amount of gypsum waste are able to be recycled because the challenges of contamination with other materials during manufacturing process. It required further research and development for application of gypsum waste (Euro Gypsum,2007).

2.3 Dental Gypsum

Gypsum, which is use in dentistry is calcium sulphate hemihydrate $(CaSO_4)_2 \cdot H_2O$. Its main uses in cast, modelling and making it to become mould. Impression materials are recorded as the morphology of the hard and soft tissues of patient and subsequently slurry gypsum will be poured into the impression, then it will become harden to form a rigid replica model mould according to the morphology of the hard and soft tissues of patient. (McCabe & Wall, 2008)

Dental stone used as dental mould are produce by two methods. One method is heating gypsum in 125 °C in autoclaving process with steam condition, it will form α-hemihydrate. The other alternative method is gypsum boiled in a solution of a salt such as $CaCl_2$ and undergo autoclaving process. The color of dental stone are pale yellow or green color. It enables user to distinguish it from dental plaster which is white color although the chemical properties of dental plaster and dental stone are same (McCabe and Wall, 2008).

Figure 2.2: Dental stone in powder form (McCabe and Wall, 2008)

2.4 Calcium Phosphates Family

Calcium Phosphates(CaP) are main constituents inside tooth and bone of human body. CaP is suitable to repair the damage bone in human body because human's bone consist of 70% of calcium phosphates. CaP is 'old biomaterials',but still haveing higher potential in future biomaterials application (Habraken .et al,2016). In Table 2.1, it simplified the calcium phosphate family members including biphasic calcium phosphate (BCP), amorphous apatite (APT), carbonated hydroxyapatite (CHA), calcium-deficient hydroxyapatite (CDHA), dicalcium phosphate dihydrate (DCPD), chlorapatite (CLAP), hydroxyapatite (HA), fluorapatite (FHA), octa calcium phosphate (OCP), monocalcium phosphate monohydrate (MCPM), tetra calcium phosphate (TTCP) and tricalcium phosphate (TCP)

Table 2.1: Different types of calcium phosphate apatite ceramics (Ezuddin,2016)

Type of CaP	Chemical formula	Ca/P ratio	Crystal structure	Density
Amorphous apatite	$Ca3(PO_4)_2 \cdot nH_2O$	1.50	Amorphous	3.14
Biphasic calcium phosphate	$(1\text{-}x)\ Ca_{10}(PO_4)_6(OH)_2 + 3x\ Ca3(PO_4)_2$	Dependent on ratio of HA and β-TCP	Hexagonal and rhombohedral	3.07 – 3.21
Calcium deficient hydroxyapatite	$Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}$ [x is between 0 to 1]	1.50 - 1.67	Hexagonal	3.16
Carbonated hydroxyapatite	$Ca_{10}(PO_4,CO_3)_6(OH)_2$	Non-stoichiometric	Hexagonal	2.80
Chlorapatite	$Ca_{10}(PO_4)_6Cl_2$	1.67	Hexagonal	3.17 – 3.18
Dicalcium phosphate dihydrate	$CaHPO_4.2H_2O$	1.00	Monoclinic	2.31
Fluorapatite	$Ca_{10}(PO_4)6F_2$	1.67	Hexagonal	3.10 - 3.20
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	1.67	Hexagonal	3.14 – 3.21
Monocalcium phosphate monohydrate	$Ca(H_2PO_4)_2.H2O$	0.50	Triclinic	2.58
Octacalcium phosphate	$Ca_8H_2(PO_4)_6.5H_2O$	1.33	Monoclinic	2.61
α - Tricalcium phosphate	$Ca_3(PO_4)_2$	1.50	Monoclinic	2.87
α' - Tricalcium phosphate	$Ca_3(PO_4)_2$	1.50	Hexagonal	2.70

β - Tricalcium phosphate	$Ca_3(PO_4)_2$	1.50	Rhombohedral	3.07
Tetracalcium phosphate	$Ca_4P_2O_9$	2.00	Monoclinic	3.06

2.4.1 Hydroxyapatite

Hydroxyapatite (HA) is a predominant mineral component found in coral and human bones. Since 1960, it became potential candidate used for forming bone graft in tissue engineering. HA has been highly recommended in surgical reconstruction of bones due to its good biocompatibility, able biodegradability and osteoconductivity which suitable in human body. HA could be coated at the surface of titanium and its alloy, thus enchance the osteointegration with the host tissue (Krishnamurithy, 2013).

Hydroxyapatite has unit cell lattice parameters a = 0.94nm and c = 0.68 nm. It has a hexagonal symmetry; its unit cell can be considered to be arranged along the c-axis. Hence, the lattice structure preferred orientation that gives rise to an oriented growth along the c-axis and causes it to have needle-like morphology. It has low fracture toughness and mechanical strength; however, it has strong biological fixation to bony tissues (Al-Sanabani, 2013).

Hydroxyapatite(HA)($Ca_{10}(PO_4)_6(OH)_2$) can be produced though natural or synthesis methods. Marine coral, can mimmick cancellous bone, with chemical composition of HA similar to natural bone. Conversion of calcium carbonate skeleton of coral by hydrothermal reaction can produced Hydroxyapatite. Besides that, bovine bone after de-fatting reaction subsequently continue with calcination and hydrothermal process is other way to produce hydroxyapatite. Chemical reaction of calcium and phosphate elements able to produce hydroxyapatite with chemical-precipitation methods. One of the example is di-ammonium hydrogen phosphate salts and Calcium nitrate precipitated from the aqueous solutions to produce precipitated hydroxyapatite. Calcium and phosphorus in molecular level using sol-gel methods could produced pure hydroxyapatite (Krishnamurithy, 2013).

Hydroxyapatite (HA) is used in enhancing the bone healing. It is regarded as exclusive osteoconductive material for using in scaffolds application. HA is also applied as coating material in both orthopedic and dental implants, intrabony periodontal pockets, restoration of edentulous atrophic ridges, under and around failing subperiosteal metal implants, HA become filler for reinforcing dental resins and ridge augmentation prior to implant for metal prosthetics tissues (Al-Sanabani, 2013).

2.4.2 Tricalcium phosphate

Tricalcium phosphate (TCP) exists in many polymorphs, including α, β, γ, and super-α polymorphs. Only two polymorphs phases (α and β) of tricalcium phosphate can be used as biomaterials (Al-Sanabani, 2013). α- and β-TCP are used in several clinical applications in maxillo-facial surgery, orthopaedics and dentistry. α-TCP is the major constituent of the powder component of various hydraulic bone cements. β-TCP is the component of several commercial bi- or monophasic in composite and bio ceramics (Carrodeguas and Aza, 2011).

Dickens and Brown (1972) related α- TCP crystalline structure to mineral glaserite ($K_3Na(SO_4)_2$. Yashima and Sakai (2003) defined that α- TCP crystalline structure is monoclinic system. It belongs to the space group $P2_1/a$. Ca and PO_4 ions constituting the unit cells of α-TCP with its polymorphs packed in columns along the [0 0 1] direction. The structure of β-TCP is more densely packed than α-TCP, and more densely than α'-TCP, as shown by the calculated theoretical density (D_{th}) and volumes per formula unit (V_0) of the three substances. The difference in packing densities of the three TCP polymorphs is consistent about stability temperature ranges and their thermodynamic considerations.

Tricalcium phosphate (TCP) is a material that behaves as osteoconductive materials, which permits bone growth on their surface, into pores, pipes or channels of bones. It is biocompatible material with human body and useful for suitable inducing hard tissue formation of human body. It is a resorbable phase calcium phosphate which enable it to exhibit some good properties for support bone growth. Application of tricalcium phosphate are in cleft palate, capping agent, apexification, apical barrier, implants coating and recovering vertical bone defect. However, TCP is hard to control in sintering process resulting it to have low resistance to crack-growth propagation and poor mechanical strength. At the same time, the solubility of the TCP coating and rate of resorption of tricalcium phosphate is fast and uncontrolled will cause earlier failure in application (Al-Sanabani, 2013).

2.5 Mechanical Processing and Comminution

Dental Stone were collected in form of mould. It required reduction in size to produce smaller the size of particles, larger surface area of that particles. Larger surface of particles will easily undergo chemical reaction to the research purpose. Metso (2015) suggested that it required 2 stages of crushing for reduction size of dental stone. The two stage of crusher is primary crusher and secondary crusher. After two stages of crusher process, dental stone will undergo Milling process to achieve fine waste dental stone powder as possible. After milling process, dental stone powder will undergo sieving and the dental stone powder which size is less than 100µ is collected for uses for experiment for further stages.

2.5.1 Crushing Technique

2.5.1.1 Primary Crusher

In mineral processing technology, process of size reduction in mineral ore is very important, because this process able separated the minerals from its host rock for obtaining the mineral which commercial interested for its application. Most mineral in form of big rock, some of these mineral like ilmenite or rutile and heavy metal mineral found out in among of sand in beaches or in riverbeds. So that, it required crush if want to access that mineral by make it become ground or smaller size. Reduce sizes of rock by crushing and grinding was the first step in recovery process of minerals from the host rocks, which able to maximise the liberation of the mineral from the host rock. In primary crushing, it required mechanically operated equipment like jaw crushers and gyratory crusher. The mechanism of crushing is applying pressure, impact force or a combination of both.

2.5.1.1.1 Swing Jaw Crusher

Swing jaw to impart an impact on a dental particle placed between a fixed and the movement plate make by hardened steel. Both plates are bolted on to a heavy block. The moving plate is pivoted at the top end (Blake crusher) or at the bottom end (Dodge-type crusher) and connected to an eccentric shaft. In universal type of crushers, the plates are pivoted in the middle so that both the top and the bottom ends can move (Gupta and Yan, 2006) . This three type of jaw crusher shown in Figure 3.

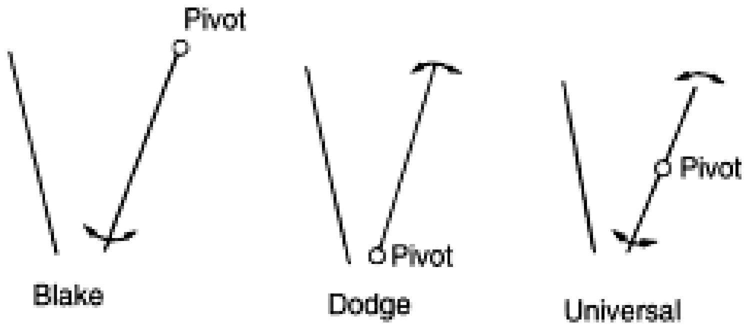

Figure 2.3: Types of jaw crusher (Gupta and Yan,2006)

The jaw crusher squeezes dental stone between two surfaces, one of which opens and closes like a jaw. Dental stone enters the jaw crusher from the top. Pieces of dental stone, that are larger than the opening at the bottom of the jaw, which lodge between the two metal plates of the jaw. The closing and opening action of the movable jaw against the fixed jaw continues to reduce the size of lodged pieces of dental stone until the pieces of dental stone are small enough to fall through the opening at the bottom of the jaw.

2.5.1.2 Secondary Crusher

The jaw crusher squeezes dental stone between two surfaces, one of which opens and closes like a jaw. Dental stone enters the jaw crusher from the top. Pieces of dental stone, that is larger than the opening at the bottom of the jaw, lodge between the two metal plates of the jaw. The closing and opening action of the movable jaw against the fixed jaw continues to reduce the size of lodged pieces of dental stone until the pieces of dental stone are small enough to fall through the opening at the bottom of the jaw.

2.5.1.2.1 Cone Crusher

Cone crushers were originally designed and developed around 1920 by Symons. It also often described as Symons cone crushers. As the mechanism of crushing in these crushers are like gyratory crushers because their designs are similar, but in this case the spindle is supported at the bottom of the gyrating cone instead of being suspended as in larger gyratory crushers.

2.5.2 Milling Process

2.5.2.1 Planetary Ball Mill

A planetary ball mill consists of at least one grinding jar which is arranged eccentrically on a so-called sun wheel. The direction of movement towards the sun wheel is opposite to that of the grinding jars which according ratio 1 : - 2 or 1 : - 1 or other else . It involved rotation of spinning base plate and rotating mill (Oleg et al., 2009).

Planetary Ball Mill can be milling few hundred grams of the powder at one time, depending on capacity of planetary ball mill machine. These are arranged on a rotating a special drive mechanism and supporter disk causes them to rotate around their own axes. The centrifugal forces alternately act in like and opposite directions, since the supporting disc and vials rotate in opposite directions. It will cause the grinding balls to run down the inside wall of the vial by the friction effect, then followed by the material being ground, traveling freely through the inner chamber of the vial, grinding balls lifting of by centrifugal force and media colliding the sample against the opposing inside wall by impact effect. The centrifugal force produced by the vials rotating around their own axes and that produced by the rotating support disk both acted on the vial contents, consisting of material to be ground and the grinding balls.

Planetary ball mills mainly used in laboratories for grinding sample to become very small sizes. Many types of grinding media can be used inside planetary ball mills process which is in accordance to their study. The example of grinding media like Iron, niobium, copper, titanium, zirconia, silica nitrate and so on are often used for grinding sample in planetary ball milling. The size of the grinding medium also influenced the efficiency of grinding on the sample. Large size of grinding medium suitable use for large size of feed. Besides that, large size of grinding medium increased the efficiency of grinding by increasing the transfer more impacted energy to the powder particles of larger weight of the ball. Figure 2.4 and 2.5 shows the image of planetary ball mill.

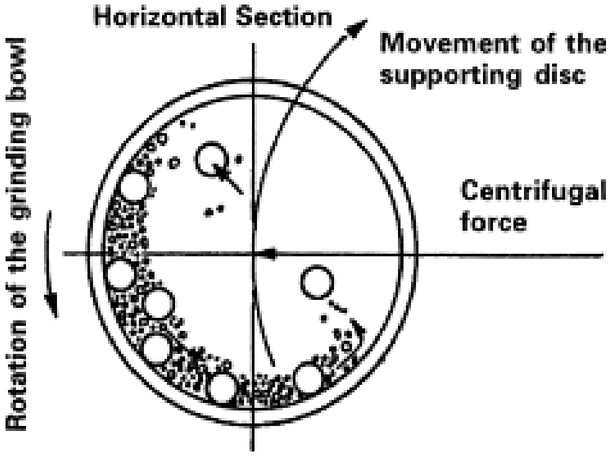

Figure 2.4: Schematic diagram of planetary ball mill depicting the ball motion inside the milling jar (Suryanarayana, 2004).

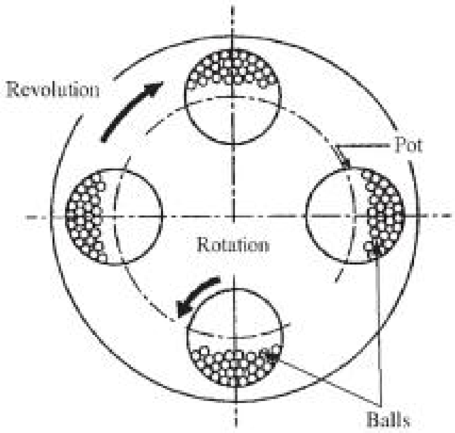

Figure 2.5: Schematic diagram of planetary ball mill illustrating the Rotation and revolution of pot (Oleg et al., 2009).

2.5.2.2 Ball Mill

Ball mill is an energy- and capital- intensive process. It more often to the tumbling types, which common the analogous for type of motion of loose grinding media . The balls sized to depend on the feed and mill size in operation and it could be different diameter by occupying 30 - 50% of the mill volume (Ozioko , 2016). Smaller balls helped to form he fined product by reducing void spaces between the balls and large balls will tend to break down the coarse feed materials. Working principle of ball mills is grinding the material by impact and attrition as the balls drop from near top of the shell. (British Expats,2013).

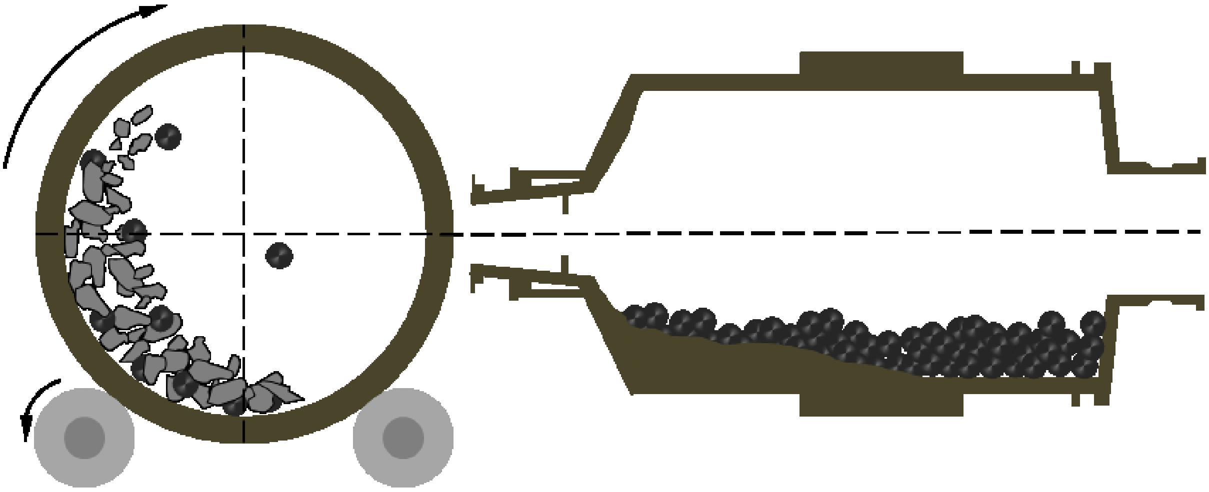

Figure 2.6: Schematic diagram of ball mill. (Hwang & et al, 2011)

2.6 Synthesis Route

2.6.1 Wet Chemical Precipitation Methods

Jarcho (1976) was the first person that investigated wet-chemical precipitation method to produce HA. He produced dense polycrystalline hydroxyapatite with a high mechanical property. After the success of his research, other researchers improved and developed this method of achieving better properties of hydroxyapatite ceramic. The factors influencing the properties of hydroxyapatite by using this method are aging time, starting materials, stirring speed, pH and temperature.

Abidi & Murtaza (2013) mention about calcium oxide (CaO), ammonium hydroxide (NH_4OH) and orthophosphoric acid (H_3PO_4) as starting materials for this method. The chemical reaction between these starting materials can obtain HA materials via this method. The reaction is mentioned in Equation 2.1 and 2.2

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (2.1)$$

$$10Ca(OH)_2 + 6H_3PO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \qquad (2.2)$$

2.7 Effect of Reaction Temperature

Researcher found that the reaction temperature has certain influence on the crystal morphology and grain structure. Crystal crystallinity of HAP phase increases significantly when temperature increased because the XRD peak is sharp and peak shape is up to its standard for rise reaction temperature from 70 °C to 95 °C. Higher temperature able enhanced the reaction kinetics for synthesis HA (Luo et al, 2015).

2.8 Effect of pH

Mohebbi and Asgary (2016) add on that some of biomaterials like hydrophilic bio cements, its physical characteristics of hydrophilic bio cements can be affected by pH value of the environment. Scanning electron microscopy (SEM) showed that bio cements have more un-hydrated and porosity structure at a pH level of 10.4. When the bio cement in acidic or highly alkaline pH levels condition, it will cause reduction of strength and hardness of the materials.

Lower pH produced powders with lower Ca/P ratios and smaller crystal size. Salahi and Moztarzadeh (2001) add on about research for composition of calcium phosphates precipitated from aqueous solution at different pH values. The research used calcium nitrate and Di-ammonium phosphate as reagent. At pH 6-8, the result shown that the present of crystalline structure of DCP and by product of Ammonium nitrate. Presence of HAP was detected by IR spectrum and XRD at pH 8-10. Ca/P ratio of product increased to 1.3 at pH 7, 8, and 9 which show it is amorphous calcium phosphate. Presence of calcium deficient hydroxyapatite when ratio of Ca/P reached 1.5 at pH 10 (Al-Qasas and Rohani, 2007).

Koumoulidis et al.(2003) add on the synthesis of HA by rapid increase in the pH value by adding concentrated NH4OH solution. Calcium chloride and Calcium Dihydrogen Phosphate was used in reagent for this research. the pH was increased rapidly from 3.22 to 8.79 and temperature was set to 97 °C. The powder was produced and aged at the above conditions for 30 mins. Non-stoichiometric hydroxyapatite able produced by Ca/P ratio equalled to 1.477 and crystallinity shown by XRD is corresponding to HAP. Due to the rapid increase in pH, product powder will have high degree of crystallinity in a supersaturated HAP solution.

2.9 Sintering

Different temperature for sintering process will cause different effect or result in morphological properties and microstructure of sintered hydroxyapatite (HAP). It also determines the effect of sintering temperature to the weight loss, total porosity of sintered compacts and appearance density of sintered HAP.

Sintering is defined as a process of removing the pores between growth and formation of strong bonds between adjacent particles with starting particles accompanied by shrinkage of component. It can be divided into three stages, which is initial stage, intermediate stage and final stage (Figure 7). The particles rearranged themselves and started to form neck at the contact points between particles of initial stage. In intermediate stage, the amount of porosity decreased substantially as necking continued to happen. The pores between each particle became closed and they were slowly eliminated by diffusion of vacancies at the pores along grain boundaries. It causes slight densification occurred at final stage (Lee and Rainforth, 1994).