CHAPTER 1

INTRODUCTION

1.1 Project Background

Silicon Carbide (SiC) also known as carborundum is an important non-oxide ceramic compounded of silicon and carbon with chemical formula of SiC. It is inorganic and non-metallic materials which typically crystalline in nature and contain metallic and non-metallic elements and extremely rare occurs in nature. SiC falls under advanced ceramics which are materials that possess exceptional properties in mechanical, chemical and oxidation resistance, thermal stability, electrical and optical behaviors by controlling their composition and internal structure. SiC is composed of tetrahedral of carbon and silicon atoms with strong bonds in the crystal lattice to produce very hard and strong material. Silicon carbide ceramics with little grain boundary impurities maintain the strength to high temperature approaching $1600^{o}C$ with no strength loss These superior qualities make SiC a perfect candidate for abrasion and cutting application as the grains of silicon carbide can be bonded by sintering to form very hard and stable ceramics. It is high potentially useful for high power and temperature materials such as electronic device due to its high hardness and good thermal and oxidation resistance.

Silicon never occurs freely in nature but in combination with oxygen forming silicates and oxides. There are two major sources of silicon raw materials economically useful for synthesis of low cost silicon for photovoltaic applications. Silicon oxide (SiO_2) is the primary source of silicon which also known as silica that is stable and relatively pure form that can be found in almost mineralogical rocks. The secondary source of silicon is silicon precursors that is widely use in technological processing industries. Lately, the sources of silica and silicon in natural and biomass resources such as rice husk and palm waste are

being researched intensively for several industrial applications. Most biomass resources are waste product that cause environmental effects, hence the development in usage of the waste resources support the sustainable development concerns.

1.1.1 Properties of Silicon Carbide

Silicon is the second member of the group IV A elements in Periodic Table of elements and has the electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^2$. Figure 1 below shows a diamond cubic lattice structure when silicon crystallizes at atmospheric pressure. Each silicon atom forming bond with four neighbouring atom.

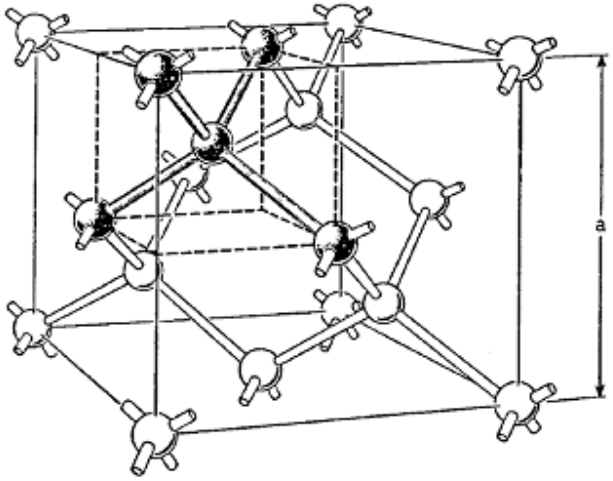


Figure 1: Diamond cubic lattice of crystalline silicon [1]

Silicon carbide has a lot of polytypes depending on the difference in the Si-C pair stacking. For example, 3C-, 4H-, 6H- and 15R-SiC are shown in Figure 2 where the leading numbers denote the repetition of SiC pair with C, H, and R representing cubic, hexagonal and rhombohedral crystal respectively.

The technology of the SiC crystal growth has been improved to have high grade crystal. SiC has become attention for its interesting characteristics as a semiconductor and it has a wide band gap ranging from 2.4 – 3.1 eV for cubic, 3C to hexagonal, 4H. Hence, it can be used in higher temperature condition. Besides, this material has a high breakdown voltage which enable device to function at high electric fields.

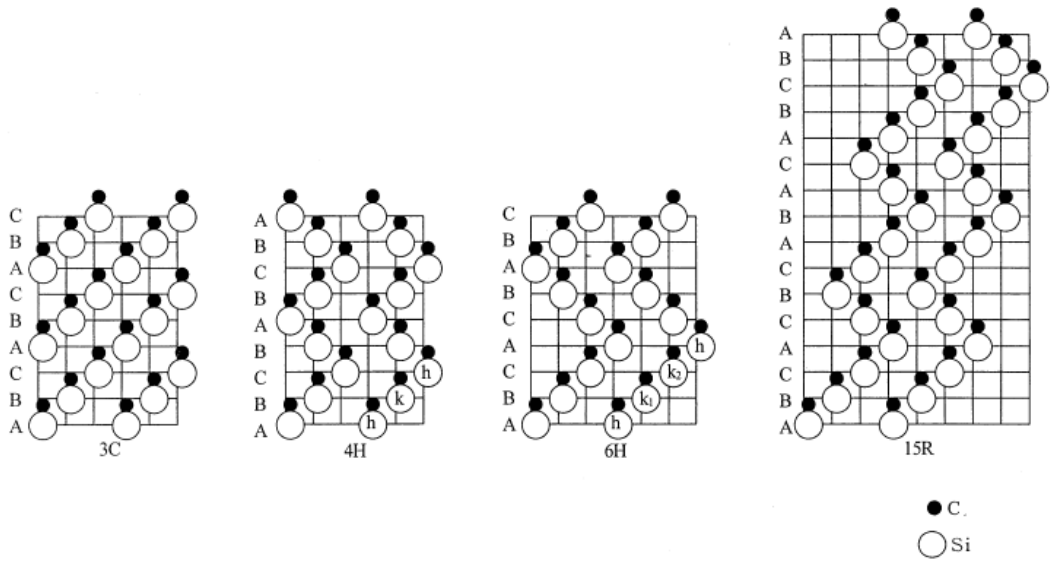


Figure 2: Crystal structure of 3C-, 4H-, 6H- and 15R-SiC [2]

1.1.2 SiC single crystals growth

Silicon carbide material has been produced through several methods of crystal growth including bulk crystal growth, epitaxial growth and hetero epitaxial growth. . Here, the brief idea of crystal growth methods is explained.

Bulk crystal growth - From Fig. 3, it is clear that SiC crystals are hard to grow from SiC melt, however can be obtained in different polytypes by a sublimation method. In this method, SiC raw materials are set at higher temperature side of furnace and a seed crystal is set at lower temperature region. After that, SiC is substrated by sublimation to obtain a bulk SiC crystal. However, the problem occurs in SiC crystal is that the existence of micro pipe than can be more than μm in diameter and could continue to a whole crystal from a seed.

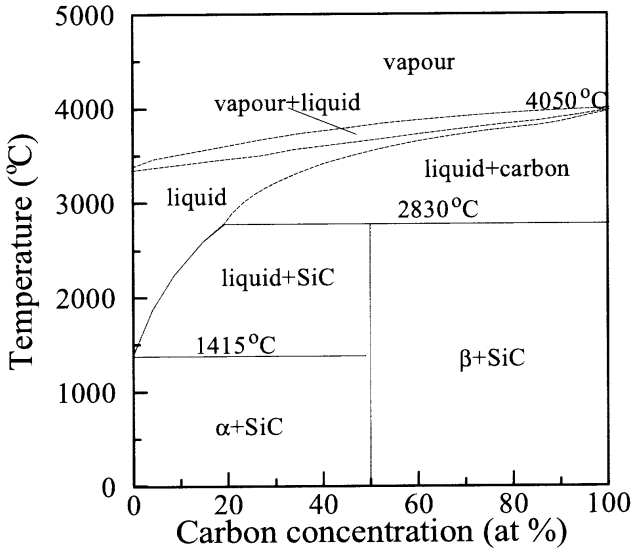


Figure 3: Phase diagram in Si-C system [3]

Epitaxial growth – Epitaxial silicon carbide is prepared by either liquid phase epitaxy (LPE) or chemical vapor deposition (CVD). In LPE, silicon melt is used as liquid but this method is less utilized because of the difficulty to control the molten silicon. On the other hand, CVD method is a typical method to obtain an epitaxial film of SiC which uses gases.

Hetero epitaxial growth – The hetero epitaxial growth has been realized by the introduction of buffer layer [4]. This layer is formed by introduction of carbon gas with Hydrogen in a furnace where single crystal Si substrate is set.

1.2 Problem Statement

The production of SiC material from natural resources are being intensively research due to its high potential used in industry and many other applications. SiC has the superior qualities over several materials which attract high demands in abrasive, cutting applications and electronic devices. However, there are numbers of method available in synthesizing SiC whereby every processing methods exhibit different characteristics of SiC products. Further study, investigation and experiment are needed to get the suitable synthesizing process that will produce SiC with acceptable high quality and good properties with an efficient and low cost production. On the other hand, the successful of SiC synthesis using the recommended technique (Low energy milling and sintering) will be evaluated and proved by analyzing technique of XRD and FESEM. The development in SiC synthesis will be observed and explained in the following parts of this paper.

1.3 Objectives and Scope of Study

This project is a research and outcome base study with the objective to critically explain the development in synthesis of SiC from available natural resources using efficient and low cost production method. This study is aiming to produce nano-crystalline SiC using low energy ball milling and sintering combination technique from base materials, silica and graphite powders. On the other hand, phase analysis and microstructure behaviors of SiC products will be carried using X-ray diffraction (XRD) and Field Emission Scanning Electrom Microscopy (FESEM).

CHAPTER 2

LITERATURE REVIEW

2.1 Sources of Silicon Raw Materials

It has been identified that two main resources of raw silicon materials that are economically feasible for the synthesis of low cost silicon mainly for photovoltaic applications [5]. The primary source of silicon is silicon dioxide (SiO_2) which commonly known as silica that is available in abundant and easily to process. Among the known polymorphs of silica, quartz and quartzite rocks are the most stable and relatively pure form that can be found in almost all mineralogical rocks [6]. Some silicon is also extracted from other silicate minerals like talc and mica

Nowadays, the sources of silica and silicon in natural biomass resources such as rice husk and palm waste are being researched extensively for certain industrial applications [7]. Hence, the development uses for these waste resources are commonly agreed with global interest towards sustainable development.

2.1.1 Silica dioxide (SiO_2)

Silica dioxide also known as sand is one of the most abundant resources and is considered the most important material in the production of glass and ceramics. It is composed of silicon and oxygen and free silica can be found in crystallographic forms depending on temperature and pressure. At atmospheric pressure, pure silica will crystallize into three mineral structures; quartz, tridymite and cristobalite [8]. Sands are good example of commercial silica that is mined as unconsolidated beach deposits, cemented sandstones or quartzite. The resistance of silica materials to thermal shock, chemical attack and mechanical wear permits them to be used in refractory products such as bricks and kiln. Silica sand can be used to make a feedstock for refined silica products such as elemental silicon metal, silicon carbide, silica glass and gels.

Particles size of sand normally range in diameter from 0.0625 mm to 2 mm. Gravel particle ranging from 2 mm up to 64 mm and silt particles are smaller than 0.0625 mm. the composition of sand is variable depends on the rock sources and conditions. Table 1 shows the important properties of pure SiO_2

Table 1. Properties of pure SiO_2 [9]

Properties	
Density	2.0 – 2.3 gm/cm^3
Electrical conductivity	Varies widely
Breakdown field	>1E7 V/cm in thermal oxides. Can be as low as 1E6 V/cm in CVd oxides
Thermal conductivity	0.01 W/cm K
Thermal diffusivity	0.009 cm^2/sec
Coefficient of thermal expansion	0.5 ppm/K
Refractive index	1.46
Dielectric constant	3.9

2.1.2 Plant-based biomasses

One important source of raw material for production of SiC is plant-based biomasses or agricultural wastes. Plant has the highest amount of SiO_2 that naturally accumulate at the outer layer or skins since it absorb silicon to build and regenerate cell walls [10]. Furthermore, these wastes are cheap and easily available all over the world. There are many factors lead to its high potential to extract SiC. It is possible to produce SiC at lower temperature because it has high surface area and intimate contact of C and SiO_2 in the plants [11]. Additionally, plant-based waste has high calorific values in promoting self-sustaining combustion process during the pyrolysis process [12]. The research works have numerous experiments and analysis on these agricultural wastes such as rice husk, coconut shell, sugarcane leaf with rice straw, bean-curd and cotton fiber in producing SiC in whiskers and particle form. The percentage of SiO_2 present in different types of agricultural waste. However, research is being done extensively on rice husk may be due to its high silica content. Table 2 shows the percentage of SiO_2 in different types of agricultural wastes.

Table 2 Percentage of SiO_2 in different types of agricultural wastes.

Agricultural waste	**Percentage of SiO_2 (%)**
Rice husk	15 – 28
Rice straw	12.42
Sugarcane leaf	6.96
Coconut shell	3.63
Bean-curd refuse	1.2

2.1.3 Woods

The biomorphic β-SiC ceramics was produced at 1400^{o}C from pine wood impregnated with silica. While the synthesis, microstructure and selected properties of biomorphic SiC and oxide ceramics from different types of woods such as pine, eucalyptus, fir and aspen and cereal fibers are also being reported [13]. Biomorphic ceramics exhibit complex hierarchical microstructures for applications that require low specific weight and high stiffness. The cellular structure of SiC is normally produced based on two-steps process : (1) controlled pyrolisis of natural precursors, and (2) high temperature reactive infiltration of the porous carbon perform [14] . The

excellent strength and specific stiffness of biomorphic ceramics has gain attraction in wide applications

2.2 Methods of Silicon Carbide Development

Having mentioned the characteristics and criteria of Silicon Carbide (SiC) and also the potential natural resources of producing it, the following of the study will focus on the various fabrication routes of SiC, starting from the traditional Achesan process up to commercialization methods. Several alternatives methods for the SiC synthesis have been reported. An overview of the most common methods for SiC production such as physical vapour deposition, chemical vapour deposition, sol-gel,liquid phase sintering will be studied in this section.

2.2.1 Traditional Acheson Process

Traditionally, SiC materials are produced in an Acheson graphite electric resistance furnace and is shown in Figure 4 . A solid-state reaction between silica sand and petroleum at very high temperature more than 2500^{o}C allow the formation of silicon carbide [15].

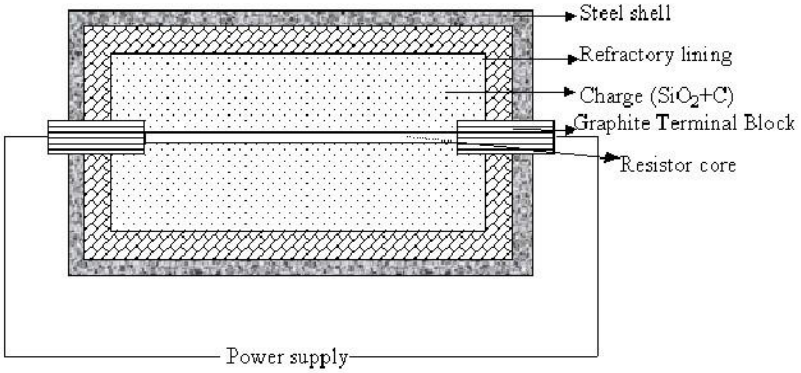


Figure 4: Graphite electric resistance furnace

$$SiO_2\ (s) + 3C\ (s) \longrightarrow SiC\ (s) + 2CO\ (g)$$

The crystalline SiC formed by Acheson method occurs in different polytypes with varies in purity. The product has a large grain size and is invariably contaminated with oxygen. Generally, SiC produced has high hardness, sharpness and good thermal properties and adequate for use as abrasive and cutting tools.

However, Acheson process is a carbothermal reduction process which needs excessive demand of energy and leads to a rather poor material.

2.2.2 Physical Vapor Transport (PVT)

Physical Vapor Transport also known as the seeded sublimation growth is a successful method to grow large size SiC single crystal. In PVT method, the control of SiC growth is difficult to control and also the adjustment of gas phase composition between C and Si species concentration is limited [16]. In overcoming this, the modified method of PVT is developed at which the source and the seed of SiC are placed in close proximity to each other and making possible the transport of the material vapor in the seed at low argon pressure.

The conventional PVT method is refined through a gas pipe conveying between the source and the crucible into the growth chamber. Taking in this new approach, a high quality of 4H and 6h-SiC crystal are growth. In order to control the gas phase composition, the modified PVT technique (M-PVT) is developed for SiC crystal preparation [17]. The modified PVT system showed the improvement of the conventional PVT system of silicon carbide.

2.2.3 Chemical Vapor Deposition (CVD)

Being the technique with largest variability of deposition parameters, CVD is the suitable method to produce SiC in various shapes of thin films powders, whiskers and nanorods using Si-C-HCI system.

The chemical reactions implicated in the exchange of precursor-to-material can include thermolysis, hydrolysis, oxidation, reduction, nitration and carboration depending on precursor species used [18].

For example, amorphous fine silicon carbide powders are prepared by CVD method in the SiH_4-C_2H_2 system under nitrogen as a carrying gas [19]. Following are the chemical equations to describe the reactions leading to SiC crystals:

$$2\ SiH_4\ (g) + C_2H_2\ (g) \longrightarrow 2\ SiC\ (g) + 5\ H_2\ (g)$$

$$CH_3SiCI + H_2 \longrightarrow CH_4 + SiCI_2 + HCI$$

$$CH_4 + SiC_2 \longrightarrow SiC + H_2$$

2.2.4 Sol-gel processing technique

Sol-gel processing techniques has gained attention because the basic advantages its synthesis approach is the production of high pure product with uniform and disperse microstructures which are not achievable using other conventional processing methods due to volatilization, crystallization and high melting temperature. Moreover the sol-gel method permits preparation of glasses at far lower temperature and has proved to be an effective way for nanopowders synthesis, adaptable to produce films, fibers and bulk pieces. Hydrolysis and polycondensation are two main steps in sol-gel process

Several approaches have been performed to improve the interest of sol-gel process such as to prepare high reactivity precursors and then to decrease the silica carbothermal recudtion temperature to increase the SiC production yield [20]. Among methods used to synthesize ceramics nanoparticles, sol-gel processing is considered to be one of the most common and effective used technique for synthesizing β-SiC with crystallite size ranging from 9 to 53 nm. The materials produce by sol-gel technique are highly porous in nature due to the evolution of gases during carbonization and carbothermal reduction of gel precursors and thus exhibit lower densities compare with the theoretical value for SiC of 3.21 g/cm^3 [21]

2.2.5 Liquid Phase Sintering (LPS)

Silicon carbide (SiC) has strong covalent bonding, make it difficult to obtain a fully dense bulk material without any sintering additives. The sintering of SiC is performed at very high temperature which could reach 2200^{o}C in the solid state with the addition of small amount of B and C [22].

The most effective sintering aid in lowering sintering temperature and providing microstructure resistant to crack propagation is by adding the metal oxides

Al_2O_3 and Y_2O_3 [23]. Addition of sintering additives contributes to dense, fined grained microstructures consequently improved the strength of sintered materials. The approach of SiC sintering in the presence of a liquid was done by pressureless sintering of SiC with AI_2O_3 combined with rare earth oxides and has attracted attention because of the remarkable combination of mechanical, thermal and chemical properties.

2.2.6 Mechanical Alloying Process

Nanostructured silicon carbide has attract attention from many and been studied intensively because of its unique properties and wide applications microelectronics and optoelectronics [24]. Among the technique that produce nanostructured materials is mechanical alloying, a good process for producing nanomaterials at room temperature with low cost at large scale. However, this process also exhibits disadvantages such as the contamination of both the milling media and the mill atmosphere.

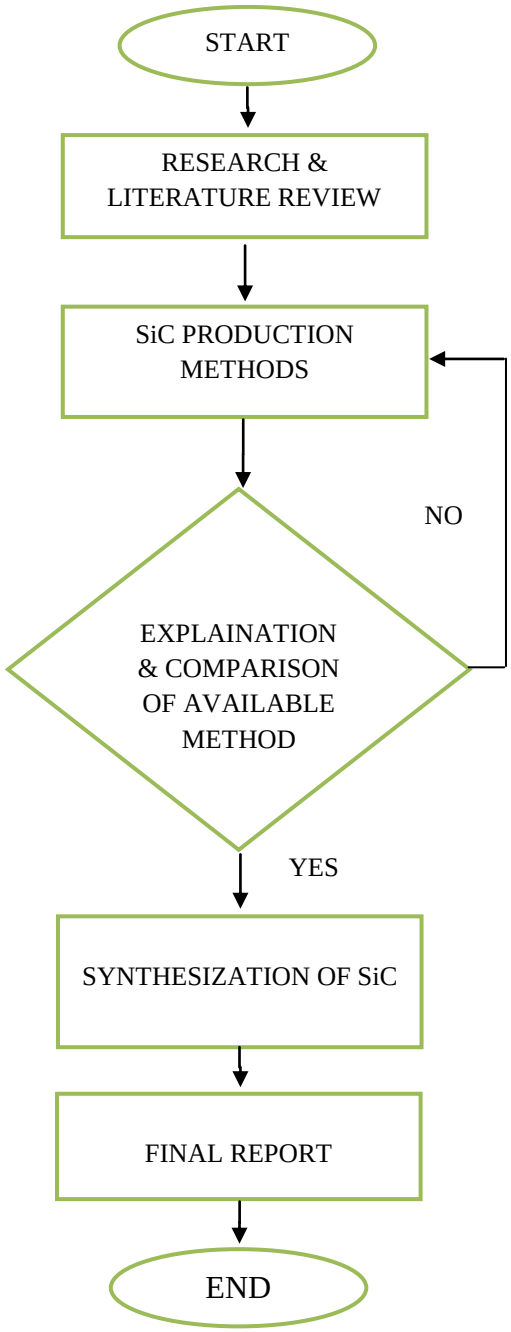
There are numerous uses of mechanical alloying and one of them is for the synthesis of nanostructured carbides. Mechanical alloying synthesized a series of metal carbides and silicates by ball milling mixtures of elemental powders at room temperature with a vibratory mill at fixed milling durations [25]. Whereas, MA used a specially build dual-drive planetary mill to synthesized nanostructured SiC starting from elemental silicon and graphite mixed in 1:1 atomic ratio [26]. Some of the important parameters that have an effect on the final powder product are:

- Type of mill
- Milling container
- Milling speed
- Milling time
- Ball-to-powder weight ration
- Temperature of milling
- Milling atmosphere

CHAPTER 3

METHODOLOGY

3.1 Project work



- Preview / Problem analysis
- Identify the fundamentals properties and applications of SiC
- Fundamental studies from references and journals

- Discover and analyze the related techniques involving SiC synthesis.
- Obtaining the fundamentals of each technique and further classification and comparison
- Identify the compatible and suitable synthesizing techniques
- Identify a specific application of targeted SiC sample
- Step to step development on SiC synthesis

- Analysis of the result
- Recommendation for further improvement
- Completion of final report

Figure 5: The work flows of the project

Silica oxide, SiO_2 compounds 46.74 % mass of silicon, Si and 53.26 % mass of oxygen. Silicon oxide exists in several forms as mentioned in the previous part of this paper, and the most common of which is low-temperature quartz. Quartz is considered having very high composition of pure SiO_2 and is colorless.

Silicon Carbide is obtained starting from high purity sands or quartz and carbon (graphite) which are reacted in an electrical furnace at 2000^0C according to the following reaction:

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

A mixture of approximately 60 percent silica sand and 40 percent finely ground graphite is charged in the furnace. Common salt is added to the mix to promote the carbon-silicon reaction and to remove impurities in the sand and graphite. During the heating period, the furnace reaches approximately 2200^oC, the point at which a large portion of the load crystallizes [27]. Finally, the silicon carbide crystals are produced together with unreacted or partially reacted raw materials. The silicon carbide crystals are removed to begin processing into aimed product.

Specimens in the form of cylindrical pellets 20 mm in diameter and 25 mm height are prepare using powder metallurgy procedure. The uniaxial pressing at 50 MPa is applied. Sintering is completed in a gas-pressure furnace with a graphite heating element in argon or nitrogen atmosphere.

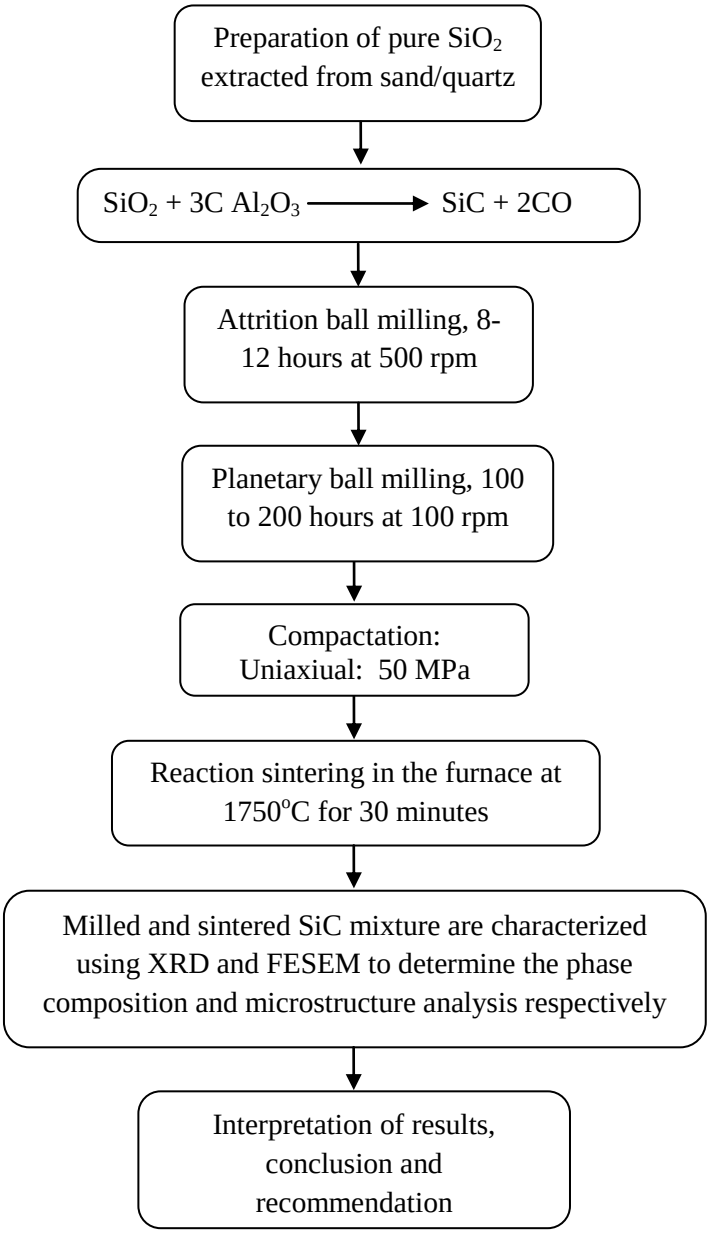


Figure 6. The flowchart of the materials processing and tests

Sintered SiC sample is characterized for phase composition and microstructure behaviors. Phase composition will be studied by X-ray diffraction (XRD). Microstructure is studied by using Field Emission Scanning Electron Microscopy (FESEM).

3.2 Materials and methods

3.2.1 Preparation of pure SiO_2 extracted from sands

Sand that is obtained from Tronoh area consists of several minerals and organic matter. It is required to separate out the impurities to have only pure sand which is silica or silicon dioxide. Washing is the simplest method of cleaning silica sand and is acceptable to produce good quality of sand grains. In the process, water is added to the sand. The movement of the slurry passing through the pipeline is sufficient to loosen the small amount of fines or clay in the ore body. After triple washing, the sand is dried under sunlight to remove water content. Next is the sizing process in order to make high quality grains of average less than 2 mm diameter separation by sieving process. For the size separation, it is important that the ground silica is void of any oversize grains.

Figure 7 Silica sands collected from an area in Tronoh

Figure 8 High purity graphite powder

Figure 9 Bigger grains of silica sands collected from an area in Tronoh. Grains size ranging from 0.5mm to 0.3 mm

Silica sand processing ball milling – A ball mill is a type of grinder used in grinding materials, in this case is silica sand. Clean silica sand grains with average diameter of less than 1 mm are loaded into the mill along with the grinding medium which is ceramic balls. It is then milled for the 5 to 6 hours until very fine grains are obtained. During ball milling process, the ball-to-power weight ratio must be taken into consideration since it is an important variable in determining final result. In the first stage of sand processing, the estimated ratio 1:20 is applied to produce silica powder. The higher the ball-to-powder ratio, the shorter the time is required. Formation of an amorphous phase was achieved in silica powder when mill for 5 hours

Figure 10 Low energy ball milling machine

Figure 11 Average size of 30-63µm silica powder after milling for 5 hours

3.2.2 Reaction Milling

Reaction milling is a process where simultaneous milling and chemical reaction takes place on highly energetic environment. It can be practiced in planetary mills where the force field could be made to vary from one to two orders of magnitude compared to equivalent size ball mills. The energy transmitted to crystalline powders during milling may result in dislocation cell structure that develops into random nanostructured grains with increasing milling time. It should be realized that even though nanometer grain size are realized during mechano-chemical processing, the particle size typically decreases only micrometer level.

3.2.3 Planetary Milling

Figure 12 shows the low energy milling machine available in the laboratory. The dual drive planetary mill consists of a gyratory shaft and two cylindrical steel jars, both are rotated simultaneously and separately at high speed. Such high speed of both jars and the shaft makes the balls to move strongly and violently, leading to large impact energy of balls that improves the grinding performance. This milling process is usually introduced for mechanical alloying (MA)

Figure 12. Planetary Low Energy Ball Milling machine

Attrition or reaction milling is carried by mixing silica powder and graphite in a milling bowl. At this stage, silicon carbide can be synthesized without heating, such as high energy milling of silica and graphite powders with addition of common salt (in this case Al_2O_3 is used) at ambient temperature which is termed as reaction milling. Reaction milling uses mechanical processing to induce chemical reactions. The energy transmitted to crystalline powders during milling may results in dislocation of cell structure that develop into nanostructured grains with increasing milling time. The milling process is easily understood by considering the motions of the balls inside the milling bowl and the individual mechanic collision including elastic and plastic deformation of the mixing powders. The composition and nomenclature of the different powder mixtures are detailed in Table 3 Reaction milling of SiC product can be done according to the following reaction:

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Table 3. Weight ratio of SiO_2 and C powder mixture during reaction milling

Sample	SiO_2: C (wt-kg)	SiO2	C	Al_2O_3
Mixture	1.5 : 1	21 g	14 g	5 g

The mechanical description of the milling process can be understood by the overall motion of the balls inside the milling chamber and the mechanics of an individual collision of the powder.

Starting materials for the milling were silica oxide, SiO_2 and graphite, C with 95 % and 99.9 % purity respectively. Milling balls of diameter 10 mm and steel jars of 10 cm diameter were used and rotate about their own axes of rotation. used for milling. Numbers of milling balls and the total mass of the powder were taken into calculation to make sure good ratio estimation. The steel ball-to-powder ratio of about 25:1. Here, silica and graphite powders were mixed in 3:1 atomic ratio. Milling was carried out for 100 to 200 hours in milling jars containing 35 g of powder mixture and 850 g of milling balls.

During this milling process, experiments were carried out for 4 hours on a continuous basis and the jar is allowed to cool to attain the room temperature.

The small sample of powder was carefully retained for size and X-ray analysis. The remaining powder was put back into the jars and the milling is continued for remaining hours. Sample will be taken at every 4 hours milling process.

However, this experiment is not to study the progress of reaction at different intervals of milling time. Powder particles were characterized by X-ray diffraction for analysis.

3.2.4 Powder Metallurgy

After the mixture of Silica oxide and graphite is mechanically alloyed by attrition milling, the powder mixture is prepared for compaction using powder metallurgy method. Granulation is taken place to ensure suitable and uniform size of pure SiC particles before proceeding with powder metallurgy. Figure 13 shows the Autopallet Press Machine in the laboratory.

Specimens in the form of block pellet are produced. The density of the pellets was determined by weighing the specimens and measuring their height and diameter while their porosity was ignored.

Figure 13. Autopallet Press Machine

For the compaction process, the load applied by Autopallet Press Machine with the maximum load applied was 50 MPa.

3.2.5 Sintering of Silicon carbide

Next important process is the heating treatment process or sintering process. Reaction sintering was completed in pressureless and normal atmosphere. Figure 14 shows the typical type of furnace for heat treatment purpose. It is also important parameter to know that the sintering process of SiC require a temperature higher than 1500^{o}C for certain hours. In this case, the sample was heat treated at 1750^{o}C held for 30 minutes. After sintering, the samples were prepared and microstructures were characterized by XRD in order to identify the intergranular phases formed of silicon carbide and to determine their chemical composition

Figure 14. Furnace used for heat treating of SiC samples

3.2.6 XRD and FESEM analysis

The resulting samples were then physically characterized using X-ray diffraction XRD) and field emission scanning electron microscopy (FESEM). XRD analysis is expected to reveal the presence of silicon carbide phases after 200 hours of low energy milling process. Meanwhile, FESEM was carried to identify a unique morphology in comparison with the starting materials.

Figure 15 The presence of SiC phase is analyzed

Figure 16 FESEM devices to carry the morphology of SiC

The project is a study base project specifically the development in silicon carbide synthesis from available natural resources that are abundantly available around Tronoh area. First and foremost, the project will begin with the research on several issues which had been mentioned in the research methodology provided.

3.3 Research Methodology

Research is a method taken in order to gain information regarding the major scope of the project. The sources of the research cover the handbook of fundamental of ceramics and silicon carbide, technical paper of previous research, e-journal and thesis and trusted links.

The steps of research:

1. Gather as many information as possible regarding the available raw materials of Silicon Carbide from natural resources.
2. Determine any possible established processing methods of SiC production from natural resources while understanding the principle, advantages and disadvantages of each methods
3. Critically study and explain each processing methods
4. Comparison among the techniques and identify the most recommended technique with low cost and good production quality.
5. Determination of a specific application of the SiC sample
6. Setting up an experiment to produce silicon carbide materials using the natural resources
7. Analysis of composition development and microstructure of the products.
8. Result interpretation, conclusion and recommendations
9. Compilation of final report

3.3 Activities/Gantt Chart and Milestone

No	Detail/Week	1	2	3	4	5	6	Mid-Semester Break	7	8	9	10	11	12	13	14
1	Selection of Project Topic: Development in Synthesis of Silicon Carbide from Natural Resource															
2	Preliminary Research Work: Research on literatures related to the topic															
3	Submission of Preliminary Report															
4	Project Work: Study on the research scope and method															
6	Submission of Progress Report															
4	Proposal defence															
8	Project work continues: Further investigation on the project and do modification if necessary															
9	Submission of Interim Report Final Draft															
10	Oral Presentation								During Study Week							

Table 4: Gantt chart and Key Milestone FYP I

No	Detail/Week	1	2	3	4	5	6	Mid-Semester Break	7	8	9	10	11	12	13	14	
1	Project Work Continues																
2	Submission of Progress Report																
3	Project Work Continues																
4	Pre-EDX																
6	Submission of Draft Report																
4	Submission of Dissertation (Soft Bound)																
8	Submission of Technical Paper																
9	Oral Presentation																
10	Submission of Project Dissertation (Hard Bound)																

Table 5: Gantt chart and Key Milestone FYP II

CHAPTER 4

RESULTS AND DISCUSSION

Generally, the mechanism of carbon-thermal reduction of Silica oxide, SiO_2 involves three reaction stages. All these three stages normally occur simultaneously in a fix period of time. Silica monoxide and carbon monoxide were obtained by direct contact in the first mixture of silica oxide and graphite.

$$SiO_2\ (s) + C\ (s) \longrightarrow SiO\ (g) + CO\ (g) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

Further synthesis will continue during the reaction milling of silica oxide and graphite to produce silicon carbide and carbon monoxide in solid and gas forms respectively. Synthesized SiO will further react with C to produce SiC by the following two reactions.

$$SiO\ (g) + 2C\ (s) \longrightarrow SiC\ (s) + CO\ (g) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

$$SiO\ (g) + 3CO\ (g) \longrightarrow SiC\ (s) + 2CO_2\ (g) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

4.1 Microstructure and phase composition analysis

4.1.1 Field Emission Scanning Electron Microscope (FESEM)

The FESEM technique was used replacing SEM technique, to conform the changes in shape and size of the milled powders during the different stages of the reaction milling process. Comparison analysis was carried for 200 h milling compacted and 200 h milling sintered SiC powder mixture. Figure 17 and Figure 19 show the FESEM micrographs of the milled compacted and sintered powder respectively.

Figure 17 shows the FESEM images of mille powders and size distribution of SiO_2 particles in milled mixture. Separate particles of SiO_2 can be seen in 200 h milled samples. The particle size of SiO_2 in milled powders has been decreased from 63 µm to 300 nm size in average by increasing milling times to 200 h. It is also observed in the FESEM morphology images that after milling process the SiO_2 particles have been covered by graphite or carbon particle. It is identified that after the milling, a small amount of milling media was mixing into the base material resulted from wearing. Assumption has been made to the weight decrease of the milling balls and jar's wall after 200 h. The FESEM study reveals the trace of alumina and other contaminants due to the wearing of the vial and also the existing amount of Al_2O_3 in powder mixture. This also can be seen in the XRD patters of milled mixture.

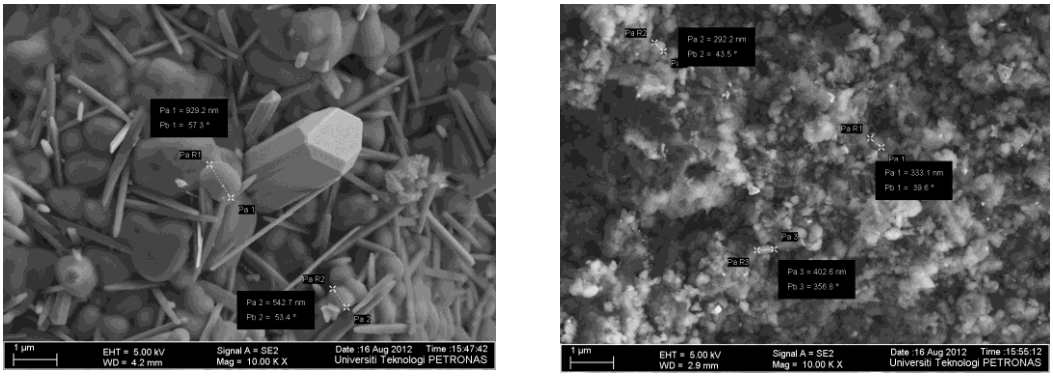


Figure 17 FESEM micrograph of the milled powders and size distribution of SiO_2 grains in milled mixture after milling time of 200 hours and after compaction.

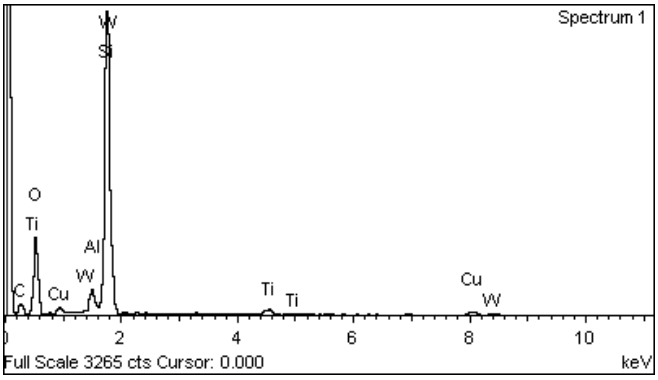


Figure 18 Spectrum processing of 200 h milled compacted sample showing the sample composition

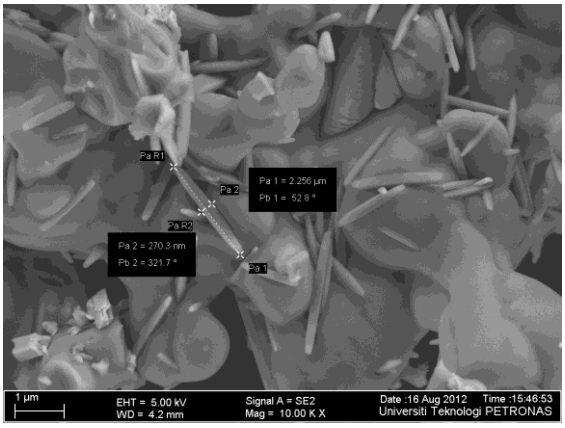


Figure 19. Image of sintered milled powder mixture which SiC is developed

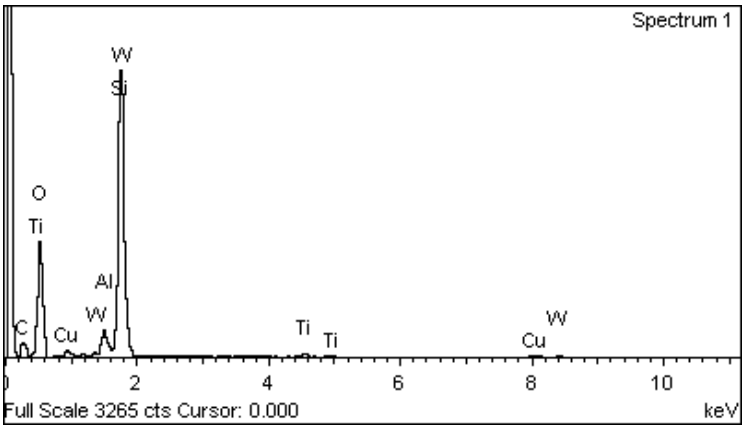


Figure 20. Spectrum processing image of 200 h milled sintered sample

Separate particles of SiO_2 can be seen in the milled sample. The particle size of SiO_2 in milled powders has been decreased from 63µm to nanometer size by increasing milling time to 200h. Indication also observed that after long milling duration the SiO_2 grains have been covered by C particles. Generally, the contacting surface area between particles of the milled mixture has been increased. It is also identified that after milling, a small amount of milling media was mixing together with base materials resulted from wearing of the milling balls and jar's wall. The FESEM study reveals the trace of alumina and other contaminants due to the wearing of the vial and the Al_2O_3 contents in powder mixture.There are several fundamental processes to be understood in the development of silicon carbide synthesis. The purity of the silica sands and graphite powders must be determined. Comparison has

been made to evaluate different sand qualities and purity taken from few places around study case area, Tronoh.In some of the SiC production techniques, SiC crystalline is produced at very high temperature ranging from 1800^{o}C to 2200^{o}C due to variety of particle sizes. Therefore, the ball milling process is very crucial in changing the production parameters.

4.1.2 X-ray Diffraction Analysis (XRD)

In order to determine the phase change of the particle mixture during the reaction milling process, a small sample of milled product was picked up at two different milling times of 100 hours and 200 hours for X-ray diffraction analysis. The two different patterns correspond to milled powder at different milling time are shown in Figure 21 and Figure 22 respectively.

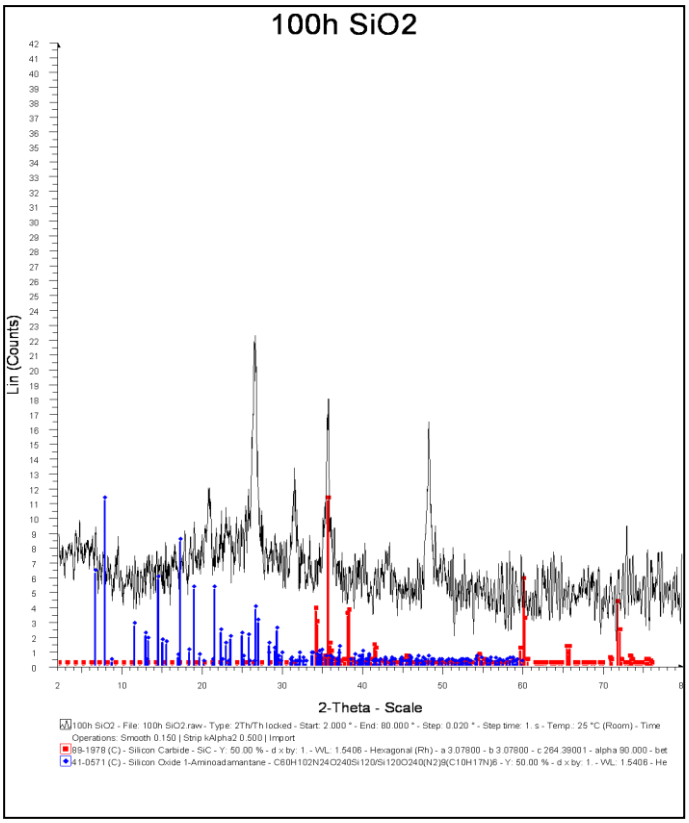


Figure 21 XRD patterns of milled powder at 100 hours of milling time for same milling parameters

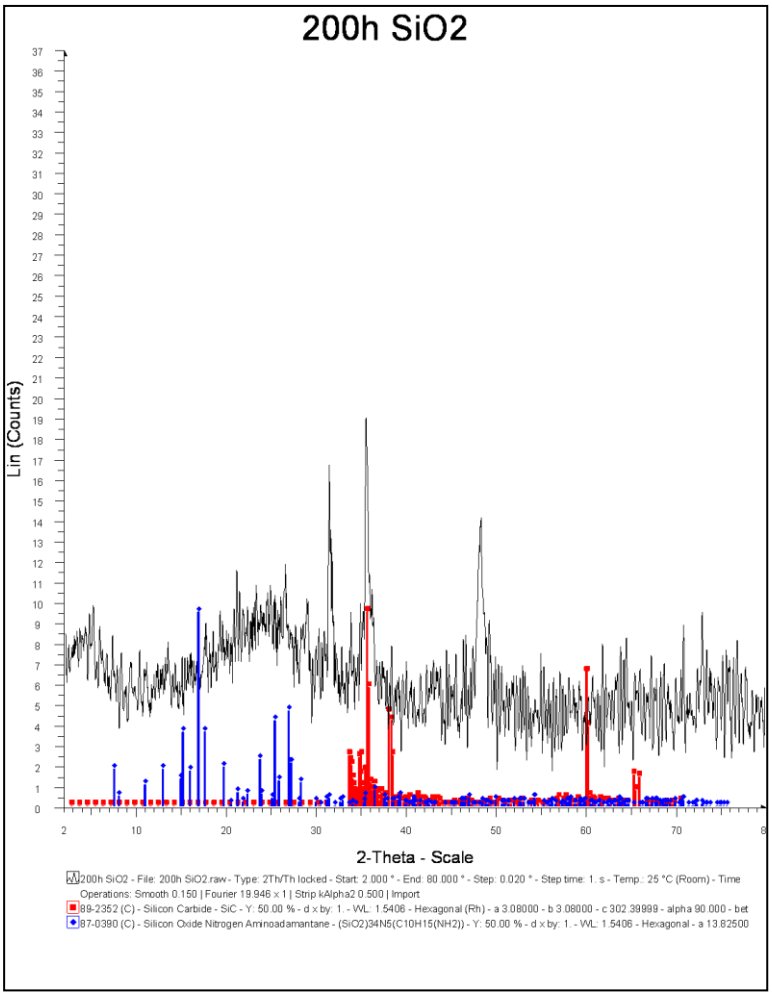


Figure 22 XRD patterns of milled powder at 200 hours of milling time for same milling parameters

From Figure 3a, silica sands collected from Tronoh are said to have rich of low and high quality quartz mineral. Other crystallize minerals were not presented in this pure silica oxide. As for 12 h milled sintered powder mixture, XRD revealed the SiC crystalline phase was not yet developed but SiO_2 and C particles were still dominating as seen in red indications in Fig. 3b. At this stage, the reaction between SiO_2 and C particles might have occurred but very insignificant as the milling hour required was not achieved.

The comparison between 100 h and 200 h milled and sintered powder mixture was critically done. Figure 3c shows a low amount of SiC phase has been formed due to 100 h milling. This is in agreement with the preliminary result that SiC phase is not fully develop at this stage. The SiC phase can be seen in red indications of the graph. There was significant amount of silica oxide which was not reduced. Significant amount of SiC was successfully produced after 200 h milling using low energy milling technique. Figure 3d shows that the presence of SiC phase is more obvious when more silica oxide has been reduced. Therefore it is proven that when extending milling time from 100 to 200 h leads to an increase in the accumulating energy in the powders and the mechanical reaction between particles is increased. The amount of SiC produced has increased in accordance with the extending milling time.

4.2 Particle Size

During the early process of milling, the powder particles of SiO_2 and graphite are mixed together and then mechanically alloyed. At later stage, the solid state reaction starts and considerable amount of the SiC product is developed. Particle sizes of the powder mixture were compared such that the reduction in particle size was observed before and after milling process. The particle size of silica and graphite powder mixture has been reduced from 30µm - 150µm to average 300 nm size after 200 hours milling time. This size continuously decreased by the increasing in milling times.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

The preparation of SiC nanometer powders were successfully fabricated in a series of experimental process involving low energy milling which has introduced the mechanical alloying and also the sintering methods. The microstructure analysis of the samples was done using XRD and FESEM in order to prove the presence of SiC phase and the morphology readings. XRD analysis technique is the crucial part in determining the presence of SiC phase thus careful procedures and parameters must be taken to obtain good analysis. The effect of milling of starting materials SiO_2 and C powder mixture on reaction behavior was studied as the main parameter. It is concluded that the reaction of the powder mixture occurs mechanically after prolonged milling. The longer time it takes for milling, the more effective reaction will occur. Apart of that, particle sizes of the powder mixture were compared and observed such that the size of the particles of SiO_2 decreased due to prolonged milling process. By using low energy milling, the nanometer size of the powder mixture was produced. The increase in reaction energy as a result of greater surface reaction will able to overcome the activation energy of SiC production at slightly lower temperature. Generally, the SiO_2 particles had been covered by C particles after 200 h of milling. The indication from FESEM proved that considerable amount of SiC products had been produced by reaction milling or mechanical alloying. A little amount of SiC particles has been produced resulted by low energy milling process for 200 h. However, the products were contaminated with slightly significant amount of alumina and others which resulted in affected quality and properties of the SiC samples.

5.2 Recommendations

In order to obtain excellent result of SiC nano-crystalline, there are some recommendations for future extension of this potential research. From the very beginning, the preparation of pure SiO_2 must be done well by taking comparison from few different types of sands from the area of study in order to select the best silica sands with high purity of SiO_2. Other than that, the selection of carbon materials should have to considered because different carboneous materials exhibit different type of carbon content though have very high quality. The used of graphite may not really suitable for this process due to its properties. Petroleum coke must be considered as the best option to produce SiC crystalline. Finally, the parameters of the energy milling process such as speed, powder to ball weight ration and also the time interval of the milling must be taken care to avoid defects and contamination of to the aimed products.

REFERENCES

1. G.R Fisher, P. Barnes, Phil. Mag B 61 (1990)
2. M. Hansen, Constitution of Binary Alloys, McGraw-Hill, New York (1985)
3. J.A Lely, Ber. Dtsch. Kerm. Ges. 32 (1955)
4. S. Nishino, H. Suhara, H. Ono, H. Matsunami, J.Appl. Phys (1987)
5. J. Dietl, Current Aspects in Low-cost silicon technology, *in Proceedings Symposium on Materials and New Processing technologies for Photovoltaic*
6. L.P Hunt,"Silicon Precursors," *in handbook of Semiconductor Silicon Technology* (1990)
7. Y. Shinohara, N.Kohyama, " Quantitative Analysis of Tridymite and Cristobalite crystallized in Rice Husk Ash by Heating, " *Industrial Health* (2004)
8. Bruvel F (1999). *Silica Sand*. Queensland Department of Mines and Energy, Mineral Information Leaflet
9. 'Structural Similarities and Dissimilarities between SiO_2 and H_2O'. F. Liebau in the physic and technology of Amorphous SiO_2,R.A Devine (1992)
10. R. Pieko, S. Paslawska, Planta Med. 27 (1975)
11. J.G Lee, Am.Ceramic. Soc. Bull. Material Science, 1987
12. M.R.b. Taib, Production of Amorphous Silica from Rice Husk in Fluidized Bed System, UTM, Johor 2007
13. D. Popovich, S.Baskaran, "Silicon Nitride and Silicon Carbide Fibrous monolithic ceramics (1994)
14. J.M. Qian, J.P Wang, "Preparation and Characterization if Biomorphic SiC Hollow Fiber from Wood by Chemical Vapor Infiltration" Scr. Material (2005)
15. Fend Z. C, (2004), Sic power materials; Devices and applications
16. Tairov M. Y, Tsvetkov V. F, (1978), Investigation of growth processes of ingots of silicon carbide single crystal, Journal of Crystal Growth

17. Wellmann P, Desperrier P, Muller R, Straubinger T, Winnack A, Baillet F, Blanguet E, Dedulle J.M, pons M, SiC single crystal growth by a modified physical vapor transport technique, *Journal of Crystal Growth*, (2005)
18. Barth S, Ramirez F.H, Holmes J.D, Rodriguiz A.R (2010), Synthesis and applications of one-dimensional semiconductors, *Progress in Materials Science*
19. Kavecky S, Anekova B, Madejova J, Sajgalik P (2000), Silicon Carbide powder synthesis by chemical vapor deposition from siliane reaction system, *Journal of the European Ceramic Society*
20. Julbe A, Larbot A, Guizard, Charpin J, Bergez P (1990), Effect of boric acid addition in colloidal sol-gel derived SiC precursors, *Materials and Research Bulletin*
21. Raman V, Bahl O.P, Dhawan U (1995), Synthesis of silicon carbide through the sol-gel process from different precursors, Journal of Materials Science
22. Izhevsky V. A, Genova L.A, Bressiani A.H.A, Bressiani J.C (2000), Liquid phase sintered SiC.Processing and transformation controlled microstructure tailoring, *Materials Research*
23. Omori M, Takei H (1982), Pressureless sintering of SiC, *Journal of American Ceramic Society*
24. Li X. B, Shi E. W, Chen Z.Z, Xiao B, Polytype formation in silicon carbide single crystal, *Diamond and related materials* (2007)
25. Le Caer G, Bauer Grosse E, Pianelli A, Bouzy E, Matteazzi P (1990), Mechanically driven synthesis of carbides and silicates, *Journal of materials science*
26. Chaira D, Mishra B.K, Sangal S (2007), Synthesis and characterization of silicon carbide by reaction milling in a dual-drive planetary mill, *Materials Science and Engineering*
27. Negita, K. Effective sintering aids for silicon carbide ceramics; reactivities of silicon carbide with various additives.

28. Bayer, R.G (1976), Selection and Use of Wear Tests for Metals, STP-615, ASTM, Philadelphia, PA

29. ASTM E10 - 08 Standard Test Method for Brinell Hardness of Metallic Materials