## SYNTHESIS OF SILICON CARBIDE BY ARC-DISCHARGE PROCESS

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ภาควิชา<u>วิศวกรรมเกม</u>ีลายมือชื่อนิสิต\_\_\_\_

สาขาวิชา<u>วิศวกรรมเคมี</u>ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก<u></u> ปีการศึกษา<u>2554</u>ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

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# PAITOON LERTSURASAKDA: SYNTHESIS OF SILICON CARBIDE BY ARC-DISCHARGE PROCESS. ADVISOR: ASST. PROF. VARONG PAVARAJARN, Ph.D., CO-ADVISOR : CHANTAMANEE POONJARERNSILP, D.Eng.,74 pp.

Silicon carbide is one of non-oxide ceramic materials which have been widely used in many in industrial applications due to its excellent mechanical properties, high thermal, and electrical conductivity, high thermal shock resistance, excellent chemical oxidation resistance, and high strength and stiffness. There are many methods used to fabricate silicon carbide such as carbothermal reduction process and sol-gel process. However, synthesis of silicon carbide is usually done by a process which consumes lots of energy for extended period of time. In this research, silicon carbide nanoparticles were synthesized by arc discharge process, which could produce the product within seconds. The anode, which was a carbon rod, was axially drilled and filled with silicon source, i.e. silicon monoxide powder. It was raised into a cylindrical-shaped cathode, which was also made from carbon rod. Both the anode and cathode were submerged in water. Upon the supply of direct current in the range of c.a. 80 A, arc discharge was induced. Nitrogen gas was continuously supplied through the cathode to carry the product from the arcdischarging zone to water. The effect of parameters .i.e., arc current, feeding gas component, gas flow rate and anode velocity were investigated to explain the mechanism of synthesis of silicon carbide by arc-discharge process.

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## **CHAPTER I**

## **INTRODUCTION**

Silicon carbide is one of the non-oxide ceramic materials which have been widely well established due to its exceptional mechanical, chemical and thermal resistance of the material. Its excellent mechanical properties, high thermal and electrical conductivity, high thermal shock resistance, excellent chemical oxidation resistance, namely high strength, wide band gap which is a favorable feature for a variable application and stiffness are widely used in many in industrial applications. In manufacturing, due to its hardness, it is used in abrasive machining processes such as grinding, honing etc. and it is laminated to paper to create sandpapers as well. For lapidary, silicon carbide is used as an abrasive because of its stamina. For electrical application, it is used in lightning arresters in electric power systems. The devices require high resistance. Because of its low thermal expansion coefficient, high hardness and rigidity, silicon carbide is a desirable mirror material for astronomical telescopes and silicon carbide is good in thermal conductivity so it is used to increase operating temperatures compared with other metallic heater. Generally,  $\beta$ silicon carbide is excellent chemical oxidation resistance so it is used as heterogeneous catalyst support. This form has already been employed as a catalyst support for the oxidation of hydrocarbons. Its high thermal conductivity, together with its high-temperature strength, low thermal expansion, and resistance to chemical reaction, makes silicon carbide valuable in the manufacture of high-temperature bricks and other refractory. It is also classed as a semiconductor, having an electrical conductivity between that of metals and insulating materials. Moreover, it an be used as filters for molten metal, semiconductor process equipment, ball valve parts, diesel particulate filter, seals or bearing, gas burner media and membrane supports for hydrogen.

Nowadays, there are many methods for producing silicon carbide power and each method is discussed in the next section. The conventional method for silicon carbide fabrication is carbothermal reduction known as the Acheson process. This process requires long reaction time and takes place at high temperature in the range of 2273-3273 K The overall reaction of the carbothermal reduction is as follow

$$SiO2(s) + 3C(s) \rightarrow SiC(s) + CO(g)$$
 Eq. (1.1)

Because of high temperature and long process, large particle size of the product is usually obtained. Milling process is required to reduce particle size to the size suitable for sintering process to produce ceramics. During the milling process, it causes unavoidable contamination of impurity into the product.

Several alternate methods to produce silicon carbide includes sol-gel technique which can produce silicon nanofiber through polymer blend technique by employing commercially available pitch as carbon [1]. The sol-gel process requires expensive precursor and complicated process.

The next method that is widely used to synthesis fine silicon carbide power is self-propagating high temperature synthesis process (SHS). The SHS process can be used to prepare a fine powder of high temperature materials at 1800 to 4000°C, using their high exothermic heats of reaction[2]. It is well known that the SHS process is a very energy-efficient method because a high temperature furnace is not required and the process is relatively simple. However this reaction cannot maintain constant temperature at any level so the reaction does not take place and the formation of a layered microstructure is occurred due to unstable displacement of the propagation wave. Other methods for synthesizing fine silicon carbide powder are thermal plasma synthesis [3] and microwave synthesis [4].However both thermal plasma synthesis and microwave synthesis require high operating cost and expensive equipments. This research investigates the synthesis of fine silicon carbide nanoparticles via arc-discharge process. This method was used to synthesize [5]. Since then, The arc-discharge in liquid have been used to synthesize many kind of fullerene related nanomaterial such as carbon nano-onions, metal-included carbon nanohorns, metal-included carbon nanotubes, multi-shelled metal chalcogenide and single-walled carbon nanotubes with nanohorn[6]. Recently Li et al, fabricated silicon carbide rods in large scale by an arc discharge technique using impure silicon carbide rod as an anode and composite graphite as cathode[7]. For arc discharge process, the reaction is taken place at high temperature (3000 - 4000 K) and the reactants are solid phase. The advantage of arc discharge method is low cost production and this method is uncomplicated and the operation time is fast.

As previously described, the reactants for arc discharge method are solid phase and the reaction is taken place at high temperature. It seems that the arc discharge conditions are the same as carbo thermal reduction process. Therefore, it is considered to be compared with carbo thermal reduction process in term of reaction equation. Furthermore, the arc discharge process is economical to produce silicon carbide powder compare with other methods.

In this research, we are going to fabricate fine silicon carbides via arcdischarge process. The main purpose of this research is to investigate and understand the process mechanism for the formation of silicon carbide, as well as the effect of the various variables and the characteristic of the synthesized silicon carbide. The scopes of this study are as follow:

- 1. For the atmosphere of the system, arc discharge will be done in liquid which is water (deionized-water).
- 2. Silicon carbide is synthesized via arc discharge process. The variables of the reaction are investigated include reactant source, ratio of the reactant, arc current, gas floe rate, anode's speed rate and various of gas injection. The arc current given to the system is in the range of 40-100 A. The overall flow rate of the gas injection and the anode's speed rate are in the range of 3-10 L/min and 0.5-1.5 mm/s, respectively. The reaction gases using in the experiment are nitrogen gas argon gas and air. The silicon source using in the process are silicon powder, silica mixed with carbon and silicon monoxide.
- 3. The synthesized silicon carbide is characterized by using powder X-ray diffraction (XRD) for identification and crystalline phase analysis. The function group is determined by using Fourier Transform Infrared (FT-IR). Transmission Electron Microscope (TEM) is used to characterize the morphology of synthesized product. Gas chromatography (GC) is also used to identify synthesized gas. Gas chromatography (GC) is also used to identify synthesized gas.

The thesis is divided into five parts. The first three parts describe general information about the study, while the following two parts emphasize on the results and discussion from the present study. The background and scope of the study are present in Chapter 1. In chapter 2 consists of theory and literature survey, while the experiment systems and procedure used in this study are shown in Chapter 3. The results of the experiment are given in Chapter 4 Finally, in the last chapter, the overall conclusion from the results are present.

## **CHAPTER II**

## THEORY AND LITERATURE SURVAY

### 2.1 Background and Properties of silicon carbide

Silicon carbide was discovered by Edward G. Acheson in 1891. In his experiment, he was attempting to produce artificial diamonds, Acheson heated a mixture of clay and powdered coke in an iron bowl, with the bowl and an ordinary carbon arc-light serving as the electrodes. And he found bright green crystals attached to the carbon electrode and thought that he had prepared new compound of carbon and alumina from the clay. So he called the new compound that Carborundum because the natural alumina is called corundum. He found that this crystal's hardness is the same as diamond. So his product was used for polishing of gems and its price was cheaper than other natural diamond dust. The new compound, which was obtainable from cheap raw materials and in good yields, soon became an important industrial abrasive.

Generally, pure silicon carbide is white or colorless. In naturally, the polymorphism of Silicon carbide is characterized by a large family of similar crystalline structures called polytypes. They are variations of the same chemical compound that are identical in two dimensions and differ in the third as shown in Fig 2.1



(β)3C-SiC





Figure 2.1Three porlymorphs of silicon carbide

The beta silicon carbide ( $\beta$ -SiC) will be formed when the temperature of the system is below 1700<sup>o</sup>C and the alpha silicon carbide ( $\alpha$ -SiC) will be formed when system temperature is greater than 1700<sup>o</sup>C. The beta silicon carbide ( $\beta$ -SiC) usually has higher surface area when compared with the alpha silicon carbide ( $\alpha$ -SiC). Therefore it is generally used in industrial applications as support for heterogeneous catalysts which is mentioned in the previous chapter.

### 2.2 Properties of Silicon Carbide Ceramics

As a consequence of the difference in crystal structure, the two forms of SiC are different in density, as well as mechanical, thermal and thermo-mechanical properties. Nevertheless, general properties of silicon carbide are listed in Table2-1 Table 2-1 Properties of Silicon Carbide Ceramics

Properties	β-SiC	α-SiC
Bandgap (cV) at 300K	2.3	>2.9
Maximum operating temperature ( ${}^{0}C$ )	873	1240
Maximum operating temperature ( ${}^{0}C$ )	873	1240
Electron mobility $\left(\frac{cm^2}{V} - s\right)$	100	600
Hole mobility $\left(\frac{cm^2}{V} - s\right)$	40	40
Breakdownfield, $E_b(10^6 V/cm)$	4	4
Thermal conductivity $\sigma_T$ (W/cm- ${}^0C$ ):	5	5
Saturated electron drift velocity, $V_{sat}$ (107 cm/s)	2.5	2.5
Dielectron constant, ε	9.7	9.7

### 2.3 Commercial Technique for producing silicon carbide material.

Silicon carbide is not found in the nature, it has to be synthesized via many various of methods. The method using to produce silicon carbide material is carbo thermal reduction method or Acheson process as well as sol-gel technique for synthesis in morphology of fiber via polymer blend technique, self-propagating high temperature synthesis process (SHS)[2]and helicon wave plasma enhanced chemical vapour deposition[8]. But all of the methods mentioned are quite expensive and complicated process.

### 2.3.1 Sol-Gel Processing

The sol-gel process is a wet-chemical technique for the fabrication of materials starting either from chemical solution or colloidal particles to produce an integrated network, which undergo hydrolysis and polycondensation reactions to form a colloid, and form sol according to Eq. (2.1) to Eq. (2.3).

$M-O-R + H2O \rightarrow M-OH + R-OH (hydrolysis)$	Eq. (2.1)
M-OH + HO-M $\rightarrow$ M-O-M + H2O (water condensation)	Eq. (2.1)
$M-O-R + HO-M \rightarrow M-O-M + R-OH$ (alcohol condensation)	Eq. (2.3)

where M and R are metal atom and alkyl group, respectively. In general, the sol-gel process involves the transition of a system from liquid "sol" into solid "gel" phase. By applying the sol-gel process, it is possible to fabricate advanced materials in a wide variety of forms, e.g. ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and extremely porous aerogel materials.

polymerization of The sol-gel metal alkoxides or certain multifunctional organic monomers leads to the formation of highly cross-linked, transparent gels. Porosity of the final products depends on the structure of their parent hydrogel, which is mostly formed during the sol-gel transition. A catalyst used in the sol-gel polycondensation usually plays the most important role for the formation of the porous structure of the hydrogel. The catalyst initially promotes the generation of resorcinol anions. These anions are subsequently transformed into substituted resorcinols, which form RF clusters through polycondensation. Then RF clusters react with each other and grow into colloidal particles, which finally form a RF hydrogel[9].

This method was used to produce silicon carbide nanofiber with sol-gel derived silica technique. Methyltriethoxysilane (MTEOS,Lancaster,98%) and QI free pith were used as silica source and carbon source, respectively. MTEOS was mixed with water and alcohol with ratio is 1:4:4 and stirred to get the silica sol. QI free pith was mixed with acetone and then add to the silica sol and stirred to get the pitch incorporated with sol-gel silica used as SiC precurer. This precursor was then carbonized at 1000<sup>0</sup>C. The true mechanism is unknown but the overall reaction of this process can be represent as a carbo thermal reduction equation as follow

$$SiO_2 + 3C \rightarrow SiC + 2CO$$
 Eq. (2.4)

The carbonized SiC precursor was analysis for carbon and silica content. The result was shown that the ration of carbon and silica was 1:4shown that the carbon was sufficient for the carbothermal reduction of silica according to previous reaction equation. This method can be used to synthesize silicon carbide nanofiber. But it is quite complicated method and production cost for this process is high. The carbo thermal reduction of silica was used for preparing silicon carbide powder. The overall reaction equation is as following:

$$SiO_2 + 3C \rightarrow SiC + 2CO$$
 Eq. (2.5)

In the process, the gaseous SiO was first formed via the following reaction:

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g)$$
 Eq. (2.6)

$$SiO_2(s) + CO(g) \rightarrow SiO(g) + CO_2(g)$$
 Eq. (2.7)

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$
 Eq. (2.8)

The reaction between solid carbon and gaseous lead to synthesize silicon carbide, the reaction equation as following:

$$2C(s) + SiO(g) \rightarrow SiC(s) + CO(g)$$
 Eq. (2.9)

The particle shape and size of carbo thermal reduction of silica synthesized SiC are determined by the carbon used as a reactant. This method was high reaction temperature and long reaction time so the synthesized product was large. Therefore, milling process was requested. Nevertheless, milling process caused contamination of power impurities[10].

# 2.3.3 Helicon wave plasma enhanced chemical vapour deposition (HW-PECVD)

Helicon wave plasma (HWP) source has many advantages, such as the higher plasma density, lower ion energy and lower working pressure, which can lead to a greater efficiency in gas dissociation such as the breaking of C–H and Si–H bonds in the feed stocks. Furthermore, the HWP can be excited apart from the processing chamber, which provides the possibility of controlling separately the reactant activation and the surface reaction process. Wei Yu et al report the synthesis of nanocrystalline 3C siliconcarbide films by using helicon wave plasma enhanced chemical vapor deposition (HW-PECVD) in H2, SiH4 and CH4 gas mixtures at a low temperature of 300 °C.

In this work, HW-PECVD was successful used to grow nanocrystalline 3C–SiC thin films on single crystalline Si substrate at a low temperature of 300 °C with SiH4, CH4, and H2as reactant. The detailed microstructure analyses indicate tha t the high intensity of helicon wave plasma is a key condition fo rdepositing nanocrystalline silicon carbide thin films at a relative low temperature. By adjusting the magnetic field, one can control the size of SiC nanocrystal and can obtain the nanocrystalline 3C–SiC thin films with an average grain size of several nanometers at  $2.0 \times 10$ –2T magnetic field. The PL of these films presents a strong blue light emission at the room temperature when being excited by the He–Cd laser with325 nm wavelength.

### 2.3.4 Self-propagating high temperature synthesis process (SHS)

This technique consists of initiating locally a very exothermic reaction within a mixture of reactive powders and to use the heat released by this reaction to obtain, in a few seconds, a complete consumption of the reactants in the whole sample. Such simple, fast and energetically economic processes, are rather difficult to control, but lead spontaneously to very porous materials. The heat released during the reaction between silicon and graphite is too small to lead to an SHS reaction, except when the ignition temperature is higher than the melting point of silicon  $(1412^{0}C)$ 

Products with very high pore contents (~80%) were obtained using a process which consisted of heating the reactive pellets in purified argon, at15<sup>0</sup>Cmin<sup>-1</sup>, up to  $1430^{0}$ C and applying a weak d.c. voltage across the sample for 20 s. The resulting electrical current was necessary for the ignition of an SHS reaction simultaneously in the whole sample. The analysis of the sample microstructure evolution all along the process has enabled the identification of the different mechanisms involved in the SiC formation. Before the SHS stage, the formation of silicon carbide, during heating from about 1325 up to  $1430^{0}$ C, is associated with a large sample expansion, which mainly determined the final pore volume fraction. The pore transfer mechanisms, which occur during the SHS stage at1430<sup>0</sup>C, have a specific influence on the pore development. Since the final pore size distribution is strongly related to silicon graingranulometry, the porosity of the porous SiC ceramic, obtained by this process, can be easily modulated.

### 2.4 Mechanism of arc discharge process

The arc discharge was widely used to produce many kinds of material in form of nanoparticles such as multi-walled carbon, carbon nano-onions, metalincluded carbon nanohorns, metal-included carbon nanotubes, multi-shelled metal chalcogenide and single-walled carbon nanotubes with nanohorn[6]. Beside,multiwall carbon naotubes and nano-onion were synthesized via this method as well [5]. Because this method eliminate complicate process and expensive machinery such as vacuum systems, reactive gases, or laser facilities as well. So it have been widely used to produce material in form of nanoparticles.

The main point of arc discharge process is reducing size of the material via evaporation-condensation process, such as from graphite to carbon nanoparticles. The mechanism of arc discharge will be explained by mean of the synthesis of carbon nanoparticles by gas-injection arc discharge in water. In the process, conventional graphites were used as cathode and anode. On end side of the cathode was drilled to form a hole with diameter of 8 mm while the other end was also drilled for feeding gas to the process[11]. The injected gas was nitrogen gas and it was flowed through the cathode. The DC power was supplied to the electrodes, while the anode was moved toward the cathode to maintain the cathode/anode distance. The arc current was adjusted to 80 A and a constant voltage of 40 V. Both were submerged in water.

The reaction was took place within the hole, in which the space within the hole was separated into 3 parts, i.e. arcing zone, quenching zone and steaming zone (for arcing in water). When the process was begun, the reaction took place and the graphite anode was evaporated. The electron at the top of anode was motivated by the current sent along the rod. It leaded to jumping of the electron from anode to cathode. The electron jumping from the anode to cathode released the energy assumed as power energy. The energy releasing from electron jumping was assemble leading to evaporation of graphite. The region in which the reaction took place was called arcing zone. During the operation, nitrogen gas was feed to the process and caused rapid quenching of the evaporated graphite by its fast transfer from the hot arc zone to cold water. The quenching zone was observed next to the arcing zone. The evaporated graphite form into graphene sheets. Theses graphene sheets were rapidly transferred from hot zone to cool zone after which self-curing process occurred. As the results, they formed into many kinds of carbon nanoparticles at the surface of the water and depositing to the bottom floating.

### 2.5 Synthesis of materials by arc discharge method

The arc discharge in liquid has been used to synthesize many kinds of nanocarbo includes nano-onions, multi-wall carbon nanotubes etc. Recently, the research fabricating single carbon nanohorns (SWNHs) by arcing in liquid nitrogen with using catalyst-doped electrode was reported. They concluded that inert gas at the arc zone is necessary to form products [6]. Since then the synthesis of SWNHs was developed. The fabrication of SWNHs via arc discharge in water with feeding nitrogen gas was investigated. The result product is high concentration of SWNHs were found in form of the powder floating on the water surface and large production rate was observed [12].

After that synthesis of SWNHs hybridized with Pd nanopartcle using nitrogen gas injected arc in water was reported[11]. The products size and their structure obtained from arc discharge process were interested. So the effected of various condition includes gas flow rate, arc current, gas component leading to the product particle size and its morphology was investigated [13]. Beside of arcing in liquid, Arcing under gas atmosphere was reported. Multi-walled carbon nanotubes were synthesis via arc discharge under nitrogen atmosphere. The yield and morphology product which influence of nitrogen pressure and flow rate were investigated as well[14]. The molybdenum disulfide (MoS<sub>2</sub>) was also produced by arc discharge. Anode drilling to fill source in was requested It showed that the nanoparticle was formed by seamless folding of MoS<sub>2</sub> sheets [15]. Silicon nanorods

sheathed in amorphous  $SiO_2$  were fabricated by arc discharge process. Instead of using graphite as anode, the silicon carbide rod was use as anode to form silicon carbide nanorods [7].

## **CHAPTER III**

## **EXPERIMENTAL**

This chapter explains the experimental procedure used in the experiment. It is separate into 3 sections. Section 3.1 is raw material preparation while apparatus set up is described in section 3.2. Synthesis of silicon carbide by the arc-discharge and product characterizations are explained in section 3.3 and 3.4 respectively.

### 3.1 Raw material preparation and apparatus set up

In the experiments, the cathode is drilled to form a hole for supplying gas to the system. The anode is drilled for filling various silicon sources in there as well. The cathode was a graphite rod, 12 mm in diameter, drilled with 8 mm diameter and 25 mm deep hole. The anode was 3 mm in diameter and 10 mm long graphite rod. The purity of graphite in both electrodes is 99.995%. A hole with 1.5-mm diameter and 6-mm depth was drilled in the anode so that the source of silicon, i.e., silicon monoxide powder, silicon, silica mixed with carbon, could be placed within the anode. The figure of drilled cathode and drilled anode are shown in the following figure:



Figure 3.1The drilled cathode



Figure 3.2 The drilled anode

# 3.2 The apparatus set up

The apparatus was set up as shown in the following figure.



Figure 3.3Schematic diagram of the arc discharge system

The apparatus for arc discharge is set up. ADC power generator was connected to electrodes providing potential and current to the system. Electrode motion-speed control was connected to anode electrode to control movement of the anode toward cathode. The gas source which is nitrogen gas, argon gas or air was provided to the system via the cathode hole. Both electrodes were submerged in the water. The container was a glass container. In the set-up, the cathode was stationary, while the anode was movable toward the cathode. The anode feeding speed was controlled by the speed controller.

#### 3.3 Synthesis of silicon carbide by the arc-discharge

While both electrodes were submerged in deionized-water or liquid nitrogen, DC current was supplied through the electrodes to generate the arc once the anode was moved into the hole of the cathode. Nitrogen gas was constantly supplied, at flow rate in the range of 3 to 10 L/min, through the hole drilled on top of the cathode into the arcing zone. During the arc, carbon and silicon source filled into the anode were vaporized and reacted together. The solid products were carried out into the surrounding water. It should be noted that the rapid quenching prevents further growth of the product.

The arc current is one of the most important variables on a synthesis of silicon carbide. In this work, the arc current was varied from 40 to 100 A while the voltage was kept constant at 40 V. On the other hand, the stability of the arc was greatly affected by the anode feeding speed. In this work, the anode raising speed was varied from 0.5 to 1.5 mm/s.

Synthesized products were collected at three different positions, i.e., on the surface of the water, at the bottom of the container and inside the cathode hole. The products floating on the surface were scooped out of the water by a spoon while the one deposited at the bottom of the container, together with that suspended in the water, were collected by filtration. The product deposited inside the cathode hole was taken out at the end of each experiment. All products were dried in an oven to eliminate moisture before characterization.

### **3.4** Characterizations of the products

After each product was collected and dried in the oven for 24 hours. The products were characterized by using various techniques, as following

### 3.4.1 X-ray diffraction analysis (XRD)

Crystalline phase identification of the products was determined from X-ray diffraction analysis, using a X-Ray diffractometer (Bruker AXS Model D8 Discover) with CuK $\alpha$  radiation. Each sample was scanned in the range of  $2\theta = 10 - 70^{0}$  with a step size of  $2\theta = 0.02^{0}$  and scan speed was 0.2 sec/step.

### 3.4.2 Fourier-transform infrared spectroscopy (FT-IR)

The function groups in the products were determined by using Fouriertransform infrared spectroscopy analysis (FT-IR). The product was mixed with KBr and formed into a thin pellet, before measurement.

### 3.4.3 Tranmission electron microscope (TEM)

The morphology of the synthesized product was examined by using a Transmission electron microscope (JSM-6400,JEOLCo.,Ltd.) at the Scientific and Technology Research Equipment Center (STREC), Chulalongkorn University.

### 3.4.4Thermogravimetric analysis (TGA)

The residual carbon content and thermal behavior of the samples were determined by using thermogravimetric analysis on a SDT Q600 instrument. The analysis was performed from temperature of 50 to 1,100°C under a heating rate of  $10^{\circ}$ C /min in 40 ml/min flow of either oxygen or nitrogen.

## 3.4.5 Gas chromotography analysis (GC)

The gaseous product was detected and identified by using gas chromothography analysis. The analysis was perform under the condition of inject temperature of  $110^{0}$ C,column temperature of  $30^{0}$ C to 70  $^{0}$ C under a hweat rate of 5  $^{0}$ C/min.

## **CHAPTER IV**

## **RESULTS AND DISCUSSION**

#### 4.1 Synthesis of silicon carbide by arc discharge

Referring to many experimental results reported in other previous work, this part investigates effect of synthesis parameters on morphology, size and mechanism of silicon carbide generated by arc discharge. Effect of arc current, gas components injected to the system, flow rate of the gas feed and anode velocity were investigated to explain the mechanism of the silicon carbide synthesis by arc discharge. For this thesis, the silicon monoxide was used as the silicon source filled in the anode hole to investigate the effect of various parameters and explain the mechanism of silicon carbide synthesis.

# 4.2 Synthesis of silicon carbide by arc-discharge with nitrogen gas injection in water

4.2.1 XRD results of the synthesized product at each collected positions

The XRD patterns of silicon carbide synthesized under the condition of nitrogen flow rate of 5 L/min, arc current of 80 A, anode velocity of 1.5 mm/s and using water as quenching media, by arc discharge at each collecting position (floating on the surface water, depositing at the bottom of the container, together with that suspended in the water and depositing inside the cathode hole) are shown in Figure 4.1. The XRD results show that the product at each collected positions are identified as  $\beta$ -silicon carbide, silicon powder and carbon(graphite). Generally, the  $\beta$ -silicon

carbide is formed under the temperature which is lower than 1500  $^{0}$ Cwhile  $\alpha$ -silicon carbide phase is formed at the temperature which is above 1500  $^{0}$ C.

From the experiment, it is suggested that silicon monoxide vapor is generated by immense heat from the arc and react with carbon to form silicon carbide in various forms. These products are carried out of the arcing zone by the supplied gas stream and quenched by the surrounding water. It seems that the XRD peaks of  $\beta$ -silicon carbide in the product collected inside the cathode are shaper and higher than those ofones collected at other positions. On the other hand, the XRD peaks of the suspended product is shaper and higher than that of the floating product. It indicates that the product collected inside the cathode hashigher crystallinity than the product at other positions while the floating product is the less crystalline.



Figure 4.1The XRD patterns of floating product (a), precipitated and suspended product (b) and product deposited inside cathode (c).

# 4.2.2 Transmission electron microscopoic (TEM) and energy dispersive X- ray spectroscopy (EDX) analysis

The morphology of the floating sample synthesized under the condition mentioned earlier can be observed by transmission electron microscopic analysis (TEM) as shown in Figure 4.2(a), in which the crystallite size which calculated by the scherer's equation is15 nm. The selected area electron diffraction result shown in Figure 4.2(b) demonstrates that the sample might be consisted as crystalline silicon carbide. The corresponding EDX spectrum (Figure 4.3(c)) reveals that the sample is composed of Si, C and O. These results attribute to the presence of crystalline phase of silicon carbide in agreement with the XRD analysis result.



Ŷ

3.00

1.50

4.50 6.00 7.50 9.00 10.50

uKa

Q.

12.00 13.50

15.0

240

160

120

80

Figure 4.2 The TEM image of the floating product (a), The electron diffraction of the floating product (b), The EDX spectrum of the floating product(c).
#### 4.2.3 Fourier transform infrared (FT-IR) spectroscopy analysis

Characteristic chemical bonding in the synthesized samples were identified from the FT-IR spectrum presented in Figure4.3. Seven distinct absorption bands were observed. The characteristic bands at about 460 cm<sup>-1</sup> is corresponding to the out of plane of Si-O bonds[16]. The bands detected at 820cm<sup>-1</sup> and the shoulder at 967cm<sup>-1</sup> are attributed to stretching vibration of Si-C.The position major band at approximately 1050 cm<sup>-1</sup> is assigned to stretching vibrations of Si-O-Si. The shoulder at about 1200 cm<sup>-1</sup> shows a stoichiometric silicon dioxide structure. The absorbtion band in the range of 1593-1628 cm<sup>-1</sup> is related to resonance C–O bonds. A broad absorbtion band, situated between 3000 and 3600 cm<sup>-1</sup> is assigned to O-H stretching vibration.



Figure 4.3FT-IR spectrum of the floating product (a), precipitated and suspended product (b) and product deposited inside cathode (c)

The absorption bands at wave number around 820 cm<sup>-1</sup> and 967cm<sup>-1</sup> confirm that the product is mainly silicon carbide. In Figure 4.4, it should be noted that the absorption band at wave number of 830 cm<sup>-1</sup> is relating to Si-N bond which corresponds to either silicon nitride (Si<sub>3</sub>N<sub>4</sub>) or silicon oxynitride(Si<sub>2</sub>O<sub>2</sub>N). In fact, most silicon nitride formed as crystal form, while silicon oxynitride could be formed in either crystalline or amorphous form. However, the XRD results indicated only the peaks corresponding to silicon, silicon carbide and carbon. So it is suggested the silicon nitride is not formed but silicon oxynitride might be formed in amorphous phase. The presence of silicon dioxide is also witnessed from the Si-O-Si stretching band at 1200 cm<sup>-1</sup>. It is suggested that silicon dioxide is the results from the decomposition of silicon monoxide. The rest of the FT-IR signals are corresponding to carbon formed from the graphite.



Figure 4.4FT-IR spectrum of the floating product (a), precipitated and suspended product (b) and product deposited inside cathode (c)

## 4.2.4 Gas chromatography (GC) analysis

The gas chromatography (GC) analysis was used to investigate the gas produced from the experiment for mechanism explanation.

For nitrogen gas feeding experiment, the GC analysis result is shown in Figure 4.5. The  $O_2$ , $H_2$ , $N_2$ and CO peaks are detected. It should be noted the experiment was operated under the condition of arc current of 80 A, gas flow rate of 5 L/min and anode velocity of 1.5 mm/s. It was noted that CO<sub>2</sub> peak was not detected but it was suggested that CO<sub>2</sub> might be occurred but it was dissolved in the water and some of them was reacted with carbon to form carbon monoxide gas (CO).



Figure 4.5The typical GC chromatogram from the gaseous product generated in the nitrogen feeding experiment.

According to XRD, FT-IR and GC analyses, the XRD peaks of silicon powder were detected, while the fuctional group of silicon dioxide was detected by FT-IR analysis. It is suggested that silicon powder and silicon dioxide are obtained from the decomposition of silicon monoxide[17]. It should be noted that silicon dioxide obtained from the silicon monoxide decomposition is presented in amorphous phase. The silicon monoxide decomposition is proposed in the Eq. (4.1)for which , the Gibbs free energy of reaction at 1497 <sup>0</sup>K is approximately -650.12 kJ/mol

$$2\text{SiO} \rightarrow \text{Si} + \text{SiO}_2$$
 Eq. (4.1)

As the result of silicon carbide detected by XRD result shown in Figure (4.1) and the presence of CO confirmed by GC analysis shown in Figure (4.5), the reactions producing silicon carbide shown in Eq. (4.2), Eq. (4.3) and Eq. (4.4) are proposed. At temperature 1773  $^{0}$ K,Gibbs energy of Eq. (4.2),(4.3) and (4.4) are -756.26, -1063, -62.83 KJ/Mol. Silicon monoxide filled in the anode is vaporized and then react with carbon to form silicon carbide and carbon monoxide gas. The vaporized silicon monoxide then reacts with synthesized carbon monoxide gas to form silicon carbide and silicon dioxide. The reaction between silicon and carbon forming silicon carbide was shown in Eq. (4.5) for which, the Gibbs energy of the reaction at 1773  $^{0}$ k are -65.29 KJ/Mol.

$$SiO + 2C \rightarrow SiC + CO$$
 Eq. (4.2)

$$3\text{SiO} + \text{CO} \rightarrow \text{SiC} + 2\text{SiO}_2$$
 Eq. (4.3)

$$\text{SiO} + 3\text{CO} \rightarrow \text{SiC} + 2\text{CO}_2$$
 Eq. (4.4)

$$Si + C \rightarrow SiC$$
 Eq. (4.5)

According to the GC analysis result, it is indicated that CO is generated during the reaction. During the operation, the reaction of silicon monoxide with carbon to form silicon carbide and carbon dioxide revealed in Eq. (4.4) might also be occurred but it might be reacted with carbon to form carbon monoxide or dissolved in the water. However, the presence of  $CO_2$  was not detected.

The silicon dioxide generated from the Eq. (4.1) and Eq. (4.3) then reacts with CO generated from Eq. (4.2) to form silicon monoxide and carbon monoxide gas according to the reaction shown in Eq. (4.6). At the temperature of 1773 <sup>0</sup>K, Gibbs energy of the reaction is -132 KJ/Mol.

$$SiO_2 + 2C \rightarrow SiO + 2CO$$
 Eq.(4.6)

According to the GC result,  $H_2$  was also detected. This synthesized gas was generated from the reaction between carbon and water to form carbon monoxide and hydrogenas shown in Eq. (4.7). Another product generated from the reaction between carbon and water was carbon dioxide as shown in Eq. (4.8) but this reaction is not confirmed because  $CO_2$  was not detected in this work. At temperature of 1773 OK, Gibbs energy of Eq. (4.7) and (4.8) are -127 and -108 KJ/mol, respectively. It should be noted that the reaction system which was located inside the cathode hole was inert atmosphere. So both of reaction was occurred at the downstream zone of the systems. The layout of each zone of the system was shown in Figure 4.5.

$$C + H_2O \rightarrow CO + H_2$$
 Eq. (4.7)

$$C + H_2O \rightarrow CO_2 + H_2$$
 Eq. (4.8)



Figure 4.6Different zone in the arc-discharge system.

The existing of oxygen was also detected by GC analysis. The reaction which generates oxygen in this experiment is shown in Eq. (4.9). However, the peak of oxygen detected was too small comparing with other peaks and some experiment, this peak was appeared but some experiment it didn't so it is suggested that the oxygen detected by the GC analysis was contaminant from the gas sampling process.

$$SiO_2 + C \rightarrow SiC + O_2$$
 Eq. (4.9)

## 4.2.5 Raman spectroscopy analysis

The results of Raman spectroscopy analysis are shown in Figure 4.7. The peak at 520 cm<sup>-1</sup> belongs to the crystalline silicon substrate. The peak which is at 796 cm<sup>-1</sup> is typical for silicon carbide[18]. The peaks which are located at 404, 607 and 698cm<sup>-1</sup> are related to silica metrix network, Si-O-Si symmetric streching and Si-OH, respectively[19]. There are two peaks which are graphite band, namely, G-peak at 1580 cm<sup>-1</sup> and disorder band, D-peak at 1330cm<sup>-1</sup>, of which their intensities will be compared. The peak which is located at 2660 cm<sup>-1</sup> exhibits G' band and two additional weaker features could also be identified in the second-order region of the spectra (2000–3000 cm<sup>-1</sup>), i.e., one at around 2470 cm<sup>-1</sup> and another at 2920 cm<sup>-1</sup>[20]. It should be noted that Si–N or Si-O-N Raman peaks appear in the 800–1100 cm<sup>-1</sup> range[21].

The G/D ratio of the carbon product in this experiment is 0.96. This ratio has been used to show the crystallinity of carbon product obtained from the experiment. In general, when the ratio of G/D is higher, the content of crystalline carbon is expected to high. As the result, at the floating position, the G-peak (graphite band) is lower than D-peak (disorder band). That indicates that the carbon obtained from this experiment is not mainly crystalline carbon but it is consisted of amorphous carbon. In general, the conventional arc-discharge process generates carbon nanotube (CNT), carbon nanohorn (CNH), single wall carbon nanotue (SWCNT), multi-wall carbon nanotube (MWCNT) and amorphous carbon. The calculated ratio of G/D was indicated that the synthesized carbon was not reacted with oxygen or hydrogen gas which can oxidize amorphous carbon. It is therefore confirmed that there is no oxygen or hydrogen in the system. The peak of oxygen detected by GC analysis could be contaminant. The G/D ratio of floating product of this experiment was 0.96.



Figure 4.7 Raman spectrum of the product of nitrogen gas feeding experiment

From the results of the experiment, it was confirmed from the results of the XRD, EDX, FT-IR, GC and Raman analysis that the  $\beta$ -silicon carbide, silicon dioxide, silicon powder and carbon (graphite) were generated by arc discharge method using silicon monoxide as silicon source filled in the anode under the condition of arc current of 80A, nitrogen flow rate of 5L/min, anode velocity of 1.5 mm/s and use water as quenching media. The crystalline form of synthesized the product was confirmed by TEM and XRD analysis and the size of synthesized silicon carbide was15 nm calculated from the Sherer'sequation.TheH<sub>2</sub>and CO gas were generated from the reaction mentioned earlier.

For primitive studying of the mechanism of the silicon carbide synthesis by arc discharge method, the arc current, gas flow rate and anode's velocity were varied. The production rate, silicon carbide rate, carbon rate and silicon dioxide rate will be discussed in the next chapter.

#### 4.2.6Effect of the arc current

The influence of the arc current using in the experiment was studied under the condition which the constant nitrogen gas flow rate and anode velocity was 5 L/min and 1.5 mm/s, respectively. The arc current was varied in range of 40, 60, 80, 100 A. This parameter was investigated to study the arc current density using in the system. The results of silicon carbide and silicon dioxide rate of experiment using arc current of 40, 60, 80, 100 A at the collected position which were floating product, precipitated product and product inside cathode were shown in Figure 4.8(a),(b), (c) and (d), respectively. It can be observed that silicon carbide rate at any collected positions were less than silicon dioxide rate. The overall silicon carbide, silicon dioxide rate of every collected position were shown in Figure 4.8(e). It can be observed in the Figure 4.8(e) that the silicon carbide rate increased with the arc current, once the current exceeds 60 A, indicating the promotion of silicon carbide formation with respect to the increased current. The silicon dioxide rate was also shown in Figure 4.8 (e). It was shown that the silicon dioxide rate was increased with arc current corresponding to the silicon carbide rate. The overall synthesized products were shown in the Figure 4.8 (f).

In case of excessively high arc current, the synthesized silicon carbide rate and silicon dioxide rate were increased because the arc current is high which is meant that arc current density provide to the system was also high so the silicon monoxide was vaporized to become the silicon monoxide vapor reacted with carbon to form silicon carbide and carbon monoxide gas via the reaction equation as shown in Eq.(4.2) and reacted with carbon monoxide gas to produce silicon carbide and silicon dioxide as shown in Eq.(4.3). The more arc current density provided, the more silicon monoxide obtained.







(c)





Figure 4.8 (a)-(d), The results of silicon carbide and silicon dioxide rate of the experiment using arc current of 40, 60, 80, 100 A at each collected position, respectively. (e) The influence of arc current on the overall collected production rate of silicon carbide, silicon dioxide of each arc current used in the experiment. (f) The influence of arc current on the overall synthesized products of each arc current used in the experiment.

# 4.2.7 Effect of gas flow rate

Figure 4.9 (a),(b),(c) and (d) show the production rate of silicon carbide and silicon dioxide of each collected position of the gas flow rate experiment of 3 L/min, 5L/min, 7 L/min and 10 L/min, respectively. The experiment was operated under the condition of nitrogen gas injection with constant arc current of 80A and anode's velocity of 1.5 mm/s. It is considered that the rapid quenching of synthesized product is indispensable to produce silicon carbide. From the results, the rate of overall collected silicon carbide production [Figure 4.9 (e)]was increased with gas flow rate. It was also seen that at each collected position, the silicon carbide rate was still less than silicon dioxide rate. The overall synthesized products were shown in the Figure 4.9 (f).

It is considered that the rapid quenching of synthesized product is indispensable to produce the silicon carbide and silicon dioxide so the silicon carbide rate was lower when the gas flow rate was low because the quenching rate cannot be high when the gas flow rate was low.







(d)



Figure 4.9(a)-(d),The results of silicon carbide and silicon dioxide rate of the experiment using gas flow rate of 3, 5, 7, 10 L/min, respectively at each collected positions. (e) The influence of gas flow rate on the overall collected production rate of silicon carbide , silicon dioxide of each gas flow rate used in the experiment. (f) The influence of gas flow rate on the overall synthesized products of each gas flow rate used in the experiment.

# 4.2.8 Effect of anode velocity

The effect of anode velocity was shown in Figure 4.10. The continuously reaction and temperature during the operation were investigated. In Figure 4.10(a),(b),(c) and (d) show the production rate of silicon carbide and silicon dioxide of each collected position of the experiment anode's velocity of 0.3 mm/s, 0.7 mm/s, 1 mm/s, 1.5 mm/s, respectively. The experiment was investigated under the condition of constant of nitrogen gas flow rate of 5 L/min and arc current of 80A.

According to the results, it indicated that the production rate of silicon carbide and silicon dioxide were increased with anode's velocity. In case when the velocity was high, the reaction and temperature during the operation are more continuous than the relatively low velocity so the reaction operating under the continuous reaction and temperature was better performed. It was showed that the silicon carbide synthesis operation under condition of continuous temperature was significant to produce silicon carbide. Figure 4.10 (e) show the silicon dioxide rate which its tendency was the same as silicon carbide tendency. The overall synthesized products were shown in the Figure 4.10 (f).

As the result, it was confirmed that the continuous temperature and reaction occurred by the arc discharge process were important for the synthesis. If the anode velocity rate was low, the reaction did not operate continuously so the product rate was lower than each one operated under the condition of continuous temperature and reaction.



(a)





(c)





Figure 4.10 (a)-(d), The results of silicon carbide and silicon dioxide rate of the experiment using anode's velocity of 0.3, 0.7, 1, 1.5 L/min, respectively at each collected positions. (e) The influence of anode's velocity on the overall collected production rate of silicon carbide , silicon dioxide of each anode's velocity used in the experiment. (f) The influence of anode's velocity on the overall synthesized products of each anode's velocity used in the experiment.

As the results of various condition of the experiments, it was observed that the rate of silicon dioxide was always much more than silicon carbide rate. So it was suggested that one of the main reaction of the silicon carbide synthesis reaction was Eq. (4.3) which silicon dioxide was reacted with carbon to form one mole of silicon carbide and two mole of silicon dioxide.

$$3\text{SiO} + \text{CO} \rightarrow \text{SiC} + 2 \text{SiO}_2$$
 Eq. (4.3)

# 4.3 Synthesis of silicon carbide by arc discharge method with various conditions

For studying the mechanism of the silicon carbide synthesis, the gas component was change to investigate the intermediate of the reaction. The argon gas was feed to the system instead of nitrogen gas for studying the effect of nitrogen gas. The moisture of water was feed to the system to investigate the effect of the water atmosphere and the condition of feeding the gas mixing of nitrogen and air was also investigated. All of the results of various conditions were compared to explain the mechanism.

# 4.3.1 Synthesis of silicon carbide by arc discharge in water method with argon gas injection

#### 4.3.1.1 FT-IR analysis of argon gas feeding experiment

Figure 4.11 shows the FT-IR analysis result of the experiment feeding the argon gas with 5 L/min to the system via cathode hole under the condition of arc current of 80 A, anode velocity rate of 1.5 mm/s and using water as quenching media. The adsorption bands detected at 460 cm<sup>-1</sup>, 820 and 900 cm<sup>-1</sup>, 1110and1220 cm<sup>-1</sup>, 1593 and 1628 cm<sup>-1</sup> and 3404 cm<sup>-1</sup>were band of Si-O, Si-C, Si-O-Si, C-O and O-H, respectively. From the data as shown in Figure 4.8, the FT-IR signal ratios between the absorption band corresponding to Si-C bond and that of Si-O bond of feeding argon gas experiment were calculated. The FT-IR signal ratios between the absorption band corresponding to Si-C bond and that of Si-O bond of feeding nitrogen gas and argon gas feeding experiment were compared and presented shown in Figure 4.12.It can be seen that the signal ratio of Si-C bondand that of Si-O bond at each collected position of the nitrogen gas feeding experiment is lower than that one of argon gas feeding experiment



Figure 4.11 FT-IR spectrum of the floating product (a), precipitated and suspended product (b) and product deposited inside cathode (c) of argon feeding experiment.



Figure 4.12 The comparison of the FT-IR signal ratios between the absorption band corresponding to Si-C bond and that of Si-O bond of the feeding nitrogen gas experiment and feeding argon gas experiment.

As the results, it was indicated that nitrogen gas was not inert gas for this experiment. That's why the ratio of Si-C/Si-O of nitrogen feeding experiment was lower than argon gas feeding experiment. The formation of silicon oxynitride  $(Si_2O_2N)$ was discussed to explain the result. In our experiment, injected nitrogen was reacted with silicon dioxide and silicon powder decomposed from the decomposition f silicon monoxide to form silicon oxynitride. The formation reaction of silicon oxy nitride was shown in Eq. (4.10). At temperature of 1773 <sup>0</sup>K, Gibbs energy of the reaction is -550 kJ/mol.

$$3Si + SiO_2 + 2N_2 \rightarrow 2Si_2N_2O \qquad \qquad \text{Eq. (4.10)}$$

To indentify the silicon oxy nitride, FT-IR and Raman was analyzed. The functional groups of silicon oxy nitride were Si-N and Si-O. In Figure 4.13 (FT-IR of nitrogen gas feeding experiment), the absorbance peak approximately 1075 cm<sup>-1</sup> was Si-O stretching mode and the absorbance peak of Si-N stretching mode was near 840cm<sup>-1</sup>. But it was difficult to see because Si-N peaks and Si-C peak which was near 820 cm<sup>-1</sup> were overlapped.



Figure 4.13 FT-IR spectra of nitrogen gas feeding experiment, Floating product (a), precipitated and suspended product (b), product deposited inside cathode (c).

Beside FT-IR analysis, Raman analysis was also discussed. The Raman peaks of Si–N (or Si–O– N) appeared in the 800–1100 cm<sup>-1</sup> [21]. These peaks were detected in the nitrogen feeding experiment (see Figure 4.6) but were not detected in argon gas feeding experiment. The Raman spectrum of argon feeding experiment was shown in Figure 4.14

As the Raman result, the G-band was lower than D-band so the ratio of G/D was also low, the ratio of G/D approximately was 0.76. That was meant the

synthesized carbon of argon gas feeding experiment was not crystal. This result was confirmed that there was no any oxygen or hydrogen for carbon oxidization in the system reaction of argon feeding experiment.



Figure 4.14 Raman spectrum of the product of argon gas feeding experiment

Other evident that was confirmed the formation of silicon oxy nitride was the decreasing of silicon dioxide rate. According to Eq. (4.10), the silicon dioxide was used to react with silicon and nitrogen in the reaction so not only silicon carbide rate was decreased but also the silicon dioxide rate was decreased. The ratio of Si-O-Si/Si-O of nitrogen feeding experiment was compared with that one of argon feeding experiment shown in Figure 4.15. It was indicated that ratio of Si-O-Si/Si-O of nitrogen feeding experiment was lower than that one of argon feeding experiment. Therefore, it was confirm that the formation of silicon oxy nitride was exactly occurred in the nitrogen feeding experiment.



Figure 4.15The comparison of the FT-IR signal ratios between the absorption band corresponding to Si-O-Si bond and that of Si-O bond of the feeding nitrogen gas experiment and feeding argon gas experiment.

# 4.3.1.2 Gas chromatograph analysis of argon gas feeding experiment

As the GC result, The peaks of  $O_2$ ,  $N_2$  and COpeaks were identified. . It should be noted that all of the experiment was operated under the condition of arc current of 80 A, gas flow rate of 5 L/min and anode velocity of 1.5 mm/s. It was observed that  $CO_2$  was not detected from this experiment t(dissolved in the water and reacted with carbon). The peak of nitrogen detected from this reaction was an impurity gas because the argon gas injected to the system was not purity (The blank test of argon feeding experiment was shown in an appendix C.). It was suggest that hydrogen gas obtained from the reaction of carbon and water which was occurred at the downstream zone (Eq. (4.7),(4.8)) which was mentioned in the result of nitrogen feeding experiment should be occurred. But the peak of hydrogen gas and argon gas was located at the same peak. The peak of oxygen was a contaminant obtained from the gas sampling process. The reaction occurred in the argon feeding experiment was the same as that one occurred in the nitrogen feeding experiment. But in the argon feeding experiment, the formation of silicon oxy nitride was not occurred. The GC curve of gaseous product was shown in Figure 4.16



Figure 4.16The typical GC curve from the gaseous product generated by the argon feeding gas experiment

# 4.3.2 Synthesis of silicon carbide by arc discharge method in water with moisture of water injection

Generally, for the arc discharge with gas injection method, the atmosphere inside the cathode hole is inert atmosphere. This experiment was designed to feed some moisture of water to the system to set up the atmosphere system which is not inert but cover with excess moisture of the water to investigate the effect of the water affected to the reaction. The experiment was operated under the condition of arc current of 80 A, anode velocity rate of 1.5 mm/s and water atmosphere was used as media.

# 4.3.2.1 FT-IR analysis of water feeding experiment

The FT-IR spectrum of the experiment was shown in Figure 4.17.The adsorption bands detected at  $460 \text{ cm}^{-1}$ ,  $820 \text{ and } 900 \text{ cm}^{-1}$ ,  $948 \text{ cm}^{-1}$ ,  $1110 \text{ and } 1220 \text{ cm}^{-1}$ ,  $1593 \text{ and } 1628 \text{ cm}^{-1}$  and  $3404 \text{ cm}^{-1}$  were band of Si-O, Si-C, Si-OH, Si-O-Si, C-O and O-H, respectively. From the data as shown in Figure 4.10, the FT-IR signal ratios between the absorption band corresponding to Si-C bond and that of Si-O bond experiment was calculated and the data as shown in Figure 4.18.

As the result, it was shown that signal ratio of Si-C/Si-O which was shown in Figure 4.18was increased when the water was feed to the system. In the nitrogen gas feeding experiment, there was not water in the system. So the hydrogen gas detected by GC analysis was obtained from the downstream zone of the reaction so the hydrogen gas would not be reacted with silicon dioxide to form silicon monoxide and water. But in the water feeding experiment, the water was feed to the system so the Eq. (4.7) and (4.8) which were reacted in the reaction zone were occurred, that was meant the hydrogen gas in the reaction zone was increased. According to hydrogen gas increasing, the hydrogen gas in the water feeding experiment was reacted with silicon dioxide obtained to produce water and silicon monoxide which its reaction was shown in Eq. (4.11) much more than in the nitrogen feeding experiment. The functional group of Si-OH (948 cm<sup>-1</sup>) was the confirmation of Eq. (4.11). The Si-OH band was obtained from the reaction of silicon dioxide and hydrogen.

$$\text{SiO}_2 + \text{H}_2 \rightarrow \text{SiO} + \text{H}_2\text{O}$$
 Eq. (4.11)

The increasing of silicon monoxide in the reaction zone was also lead to the increasing of silicon carbide. According to the increasing of silicon monoxide with increasing of silicon carbide, it was suggested that the main reaction of the silicon carbide synthesis might be Eq. (4.2) and (4.3) which silicon monoxide was reacted with carbon to form silicon carbide and carbon monoxide and silicon monoxide was reacted with synthesized carbon monoxide to form silicon carbide and silicon dioxide.



Figure 4.17 FT-IR reflectance spectrum of the floating product (a), precipitated and suspended product (b) and product inside cathode (c) of water feeding experiment



Figure 4.18The comparison of the FT-IR signal ratios between the absorption band corresponding to Si-C bond and that of Si-O bond of the feeding nitrogen gas experiment and water feeding experiment

# 4.3.2.2 Gas chromatography of water feeding experiment

As the GC result shown in Figure 19, the peaks of  $H_2$ ,  $N_2$  and CO were detected. It was also observed that the peak of  $CO_2$  was not detected. The reaction of this experiment was the same as in the nitrogen feeding experiment and the additional reaction of Eq. (4.11). The hydrogen obtained from Eq. (4.7), (4.8) was generated in the reaction zone as mentioned earlier and then it was reacted with silicon dioxide to form silicon monoxide and water via Eq. (4.11). The increasing of silicon monoxide was the main factor of the increasing of silicon carbide.

In Figure 4.20, the Raman analysis was shown. The ratio of G/D peak of floating product was high which was approximately 2.8. That was meant that crystalline carbon was obtained from the experiment. It was indicated that the synthesized carbon was activated by hydrogen so amorphous carbon was disappeared.

This result was confirmed that there was hydrogen occurred in the system reaction of the water feeding experiment.



Figure 4.19The typical GC curve from the gaseous product generated by the water feeding experiment



Figure 4.20Raman spectrum of the products of water feeding experiment

# 4.3.3 Synthesis of silicon carbide by arc discharge method in water with mixed nitrogen gas and air

The air was feed to the system to investigate to effect of oxygen to the reaction by mixing with the nitrogen gas and feeding to the system. The flow rate of nitrogen gas and oxygen were 2 L/min and 5L/min, respectively. The reaction was operated under the condition of arc current 80A, anode velocity of 1.5 mm/s and water atmosphere.

#### 4.3.3.1 FT-IR analysis of mixing gas feeding experiment

Figure 4.21 was shown the FT-IR spectrum of the experiment. It should be noted that the collected positions for this experiment were inside the cathode and at the bottom of the barrier. The adsorption bands detected at  $460 \text{ cm}^{-1}$ , 820 and 900 cm<sup>-1</sup>, 1110 and 1220 cm<sup>-1</sup>, 1593 and 1628 cm<sup>-1</sup> and 3404 cm<sup>-1</sup> were band of Si-O, Si-C, Si-O-Si, C-O and O-H, respectively. TheFT-IR signal ratios between the absorption band corresponding to Si-C bond and that of Si-O bond of mixing gas injection experiment was calculated and the data as shown in Figure 4.22.

For this experiment, the reactions that associated with this experiment were shown on Eq. (4.12) and Eq. (4.13) which carbon reacted with oxygen to form carbon monoxide including carbon dioxide. At 1773 <sup>0</sup>K,Gibbs free energy of Eq. (4.12) and (4.13) were -580.19 and -405.07 kJ/mol. But carbon dioxide gas was not detected by GC analysis. It might be reacted with carbon or dissolved in the water which was mentioned earlier. As the result, the signal ratio of Si-C/Si-O of mixing gas injection experiment was lower than nitrogen experiment. The explanation of this experiment was about carbon reaction. The carbon was also react with oxygen ( obtained from air) instead of only reacted with silicon monoxide or silicon dioxide and then form carbon monoxide and carbon dioxide and because of increasing of carbon monoxide in the system which lead to the slow operation of the reaction Eq.

(4.2) or the inversion of the reaction of Eq. (4.2) was occurred. So the signal ratio of Si-C/Si-O was decreased.

$$2C + O_2 \rightarrow 2CO \qquad \qquad \text{Eq. (4.11)}$$

$$C + O_2 \rightarrow CO$$
 Eq.(4.12)



Figure 4.21FT-IR reflectance spectrum of the floating and precipitated product (a) and product inside cathode (b) of mixing gas experiment



Figure 4.22The comparison of the FT-IR signal ratios between the absorption band corresponding to Si-C bond and that of Si-O bond of the feeding nitrogen gas experiment and mixing gas experiment

The GC curve of the gaseous product of the mixing gas (air + nitrogen gas) feeding experiment was shown in figure 4.23. It should be noted that the flow rate of air and nitrogen were 5L/min and 2 L/min, respectively. It observed that  $H_2$ ,  $N_2$ , COgas were generated during the reaction.

In Generally, the reaction of C and  $O_2$  would generate CO and  $CO_2$  via Eq.(4.12) and Eq.(4.13), respectively.

$$2C + O_2 \rightarrow 2CO \qquad \qquad \text{Eq. (4.12)}$$

$$C + O_2 \rightarrow CO$$
 Eq. (4.13)

As the result, the decreasing of carbon reacted with silicon monoxide to produce silicon carbide due to the reaction of carbon with oxygen was lead to the decreasing of silicon carbide and the increasing of carbon monoxide in the system was lead to the slow operation of the reaction of silicon monoxide and carbon. The increasing of nitrogen in the system was lead to the increasing of the formation of silicon oxynitride reaction (Eq. 4.9). That's meant some of the synthesized silicon dioxide was reacted with silicon and nitrogen to produce silicon oxynitride. Silicon dioxide was decreased so the reaction producing silicon monoxide obtained from the reaction between silicon dioxide and carbon was also decreased so the synthesized silicon oxynitride was occurred in the system was the decreasing of silicon dioxide in the experiment. The ratio of Si-O-Si/Si-O of nitrogen feeding experiment was compared with that one of Mixing gas feeding experiment shown in Figure 4.24.

The Raman curve was shown in Figure 4.25. It was observed that the ratio of G/D was high which was 3.01. This result was due to the carbon oxidation. The synthesized carbon was oxidized by oxygen injected to the system so the amorphous

carbon was oxidized and disappeared. This result was confirmed that there was oxygen in the system reaction of mixing gas feeding experiment.



Figure 4.23The typical GC curve from the gaseous product generated by the mixing gas feeding



Figure 4.24The comparison of the FT-IR signal ratios between the absorption band corresponding to Si-O-Si bond and that of Si-O bond of the feeding nitrogen gas experiment and feeding mixing gas experiment.



Figure 4.25Raman spectrum of the product of mixing gas feeding experiment

# 4.3.4 Raman spectroscopy analysis

The dependence of G/D ratio is show in table 4.8 to show the crystallinity of each product obtained from various experiment. In generally, when the ration of G/D is higher, the concentration of crystalline carbon would be expected to become higher. It was observed that that the crystalline form of the floating product was lower other position. This result was corresponded to the quantity of crystalline product at each position. As the results of the various conditions, the product inside the cathode was much more than each other position. The quantity product at precipitated and suspended position was much more than that one of the floating position but lower than the inside cathode position. This evident was confirmed the result of the various condition experiment.
	I <sub>G</sub> /I <sub>D</sub>		
Experiment	Floating product	Deposited and suspended product	Deposited inside the cathode product
Nitrogen gas feeding	0.96	1.17	3.96
Argon gas feeding	0.76	0.99	1.26
Water feeding	2.80	1.57	2.06
Air mixed nitrogen gas feeding	3.01		1.23

Table 4-1  $I_{G} \! / I_{D}$  of the experiments at each collected positions

## **CHAPTER V**

## **CONCLUSION AND RECOMMENDATION**

#### 5.1 Results of the experiment

- From XRD results, It shows that the peaks of beta-silicon carbine, silicon and silicon dioxide can be identified at every collected position (floating position, deposited and suspended position and deposited inside cathode hole position) and the experiment is under the condition of arc current of 80 A, nitrogen gas feeding of 5L/min and anode velocity of 1.5 mm/s
- For various condition which are various arc current, gas flow rate, anode velocity of nitrogen feeding experiment, It is indicated that high arc current density, high gas flow rate and continuous reaction and temperature are important factor to produce silicon carbide
- 3. As Raman spectrum result, it reveal that carbon produced by various condition of experiment was different in term of crytallinity
- 4. For GC analysis, it is found that the synthesis of silicon carbide by arc discharge process generate H<sub>2</sub> and CO gas. All of this synthesized gas is used to explain the mechanism of the process discussed in the previous chapter.

#### 5.2 Conclusion

5.2.1The effect of arc current, gas flow rate and anode velocity to the Reaction of synthesis of silicon carbide by arc-discharge process.

From the result, it could be concluded that arc current density was significant to the synthesis reaction to vaporize the silicon monoxide and carbon. The rapid quenching was important to form silicon carbide so the high gas flow rate was requested. The result of anode velocity was indicated that the reaction with continuous temperature provided to the system was highly efficient.

# 5.2.2 The mechanism of the synthesis of silicon carbide by arcdischarge process

The first step of the reaction was the silicon monoxide and carbon was vaporized and then reacted to form silicon carbide and carbon monoxide gas

 $SiO + 2C \rightarrow SiC + 2CO$ 

Then the silicon monoxide was reacted with synthesized carbon monoxide gas to form silicon carbide, silicon monoxide. It should be noted that the silicon monoxide decomposition reaction was occurred in this experiment

$$3SiO + CO \rightarrow SiC + 2SiO_2$$
  
 $2SiO \rightarrow Si + SiO_2$ 

Then silicon monoxide was reacted with carbon monoxide to produce silicon carbide and carbon dioxide

$$SiO + 3CO \rightarrow SiC + 2CO_2$$

Si powder was reacted with carbon to produce silicon carbide via the reaction as following :

$$Si + C \rightarrow SiC$$

The silicon dioxide synthesized in the experiment was reacted with carbon to form silicon monoxide and carbon dioxide. The synthesized silicon monoxide was then used to produce silicon carbide.

$$SiO_2 + 2C \rightarrow SiO + 2CO$$

During the reaction, The reaction between Si,  $SiO_2$  and  $N_2$  was produced silicon oxynitride. This results was lead to decrease silicon carbide due to the decreasing of Si and  $SiO_2$ 

$$3Si + SiO_2 + 2N_2 \rightarrow 2Si_2N_2O$$

The reaction of carbon and water generated carbon monoxide, carbon dioxide and hydrogen. Some of carbon dioxide was reacted with carbon to form carbonmonoxide.

$$C + H_2O \rightarrow CO + H_2$$
  
 $C + 2H_2O \rightarrow CO_2 + 2H_2$ 

The synthesized hydrogen was then reacted with hydrogen to form silicon monoxide and water. The increasing of silicon monoxide was lead to increase the silicon carbide.

$$SiO_2 + H_2 \rightarrow SiO + H_2O$$

In the gas mixing experiment, carbon monoxideand carbon dioxide were produced from the reaction of carbon and oxygen. The increasing of carbon monoxide in the system was lead to the decreased synthesized silicon carbide.

$$C + O_2 \rightarrow 2CO$$
  
 $C + O_2 \rightarrow CO_2$ 

#### **5.3 Recommendation for the future**

The silicon carbide could be synthesis by arc-discharge process but it is not the main product for this experiment. The synthesized silicon dioxide is the main product. Therefore hydrogen gas would be injected to the system to react with silicon dioxide to form silicon monoxide and then synthesized silicon monoxide was reacted with carbon and carbon monoxide to form silicon carbide. But it is quite dangerous reaction.

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APPENDICES

**APPENDIX** A



Figure A.1Calibration curve of ratio of (  $SiC/[SiC+SiO_2]$  )

- Synthesis of silicon carbide by arc discharge with nitrogen gas injection

Silicon carbide rate = 
$$[M_{overall}/T] * [(M_{SiO2} + M_{SiC})/M_{overall}] *$$

 $[(M_{SiC}/M_{SiC} + M_{SiO2})] * 60$ 

$$= (0.788/25) * (25.33/100) * 0.26 * 60$$

= 0.03006 g/min

# - Gibbs energy of the reaction

$$3SiO + CO \rightarrow SiC + 2SiO_2 \quad @ 1773^0K$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta G_{f,T} = \Delta H_{f,T} - T\Delta S_T$$

$$\Delta H_{f,1773}{}^{o}{}_{K} = \int_{298{}^{o}{}_{K}}^{1773{}^{0}{}_{K}} C_{p} dT + \Delta H_{298}{}^{o}{}_{K}$$

$$\Delta S_{1773}{}^{0}{}_{K} \qquad = \int_{298^{0}K}^{1773^{0}K} C_{p} / T \ dT + \Delta S_{298}{}^{0}{}_{K}$$

$$\Delta G_{rxn,1773}{}^{0}_{K} = [G_{f,SiC,1773}{}^{0}_{K} + (2^{*}G_{f,SiO2,1773}{}^{0}_{K})] +$$

$$[(3*G_{f,Si0,1773}^{0}K) + G_{f,C0,1773}^{0}K]$$

$$= [(-146.9171) + (2*(-1083.063))] +$$

$$[(3*(-246.952)) + (-513.085)]$$

$$= -1063.1 \text{ kJ/mol}$$

Synthesis of silicon carbide by arc-discharge process

- XRD pattern of the synthesized product



Figure B.1 XRD patterns of product synthesized in the experiment using silicon powder as a silicon source filled in the anode's hole. It should be noted that that sampling was collected at the surface of the water position.



Figure B.2 XRD patterns of product synthesized in the experiment using silicon powder as a silicon source filled in the anode's hole. It should be noted that that sampling was collected at the surface of the water position.

## APPENDIX C

- Blank test of gas analysis



Figure C.1 Blank test of nitrogen gas feeding experiment



Figure C.2 Blank test of argon gas feeding experiment



Figure C.3 Blank test of water feeding experiment



Figure C.4 Blank test of mixing gas feeding experiment

## VITA

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