

ผลของพารามิเตอร์ของปฏิกิริยาต่อกระบวนการคาร์โบเทอร์มอลรีดักชันและไนไตรเดชัน  
ของถ่านเคลือบสำหรับการสังเคราะห์ซิลิคอนไนไตรด์



นางสาว ฤทัยรัตน์ ปรีชายุทธศิลป์

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จุฬาลงกรณ์มหาวิทยาลัย  
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EFFECTS OF REACTION PARAMETERS ON THE  
CARBOTHERMAL REDUCTION AND NITRIDATION  
OF RICE HUSK ASH FOR SILICON NITRIDE SYNTHESIS



Miss Ruttairat Precharyutasin

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By                                    Miss Ruttairat Precharyutasin

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Thesis Advisor                 Varong Pavarajarn, Ph.D.

---

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial  
Fulfillment of the Requirements for the Master's Degree

.....                                    Dean of the Faculty of Engineering  
(Professor Direk Lavansiri, Ph.D.)

#### THESIS COMMITTEE

.....                                    Chairman  
(Associate Professor Tawatchai Charinpanitkul, Ph.D.)

.....                                    Thesis Advisor  
(Varong Pavarajarn, Ph.D.)

.....                                    Member  
(Associate Professor Suttichai Assabumrungrat, Ph.D.)

.....                                    Member  
(Assistant Professor Sarawut Rimdusit, Ph.D.)

ฤทัยรัตน์ ปรีชายุทธศิลป์ : ผลของพารามิเตอร์ของปฏิกิริยาต่อกระบวนการคาร์โบเทอร์มอลรีดักชันและไนไตรเดชันของเถ้าแกลบสำหรับการสังเคราะห์ซิลิคอนไนไตรด์. (EFFECTS OF REACTION PARAMETERS ON THE CARBOTHERMAL REDUCTION AND NITRIDATION OF RICE HUSK ASH FOR SILICON NITRIDE SYNTHESIS)  
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การสังเคราะห์ซิลิคอนไนไตรด์ซึ่งเป็นวัสดุโครงสร้างสำหรับการใช้งานที่มีความเครียดทางกลสูงภายใต้อุณหภูมิสูงได้ถูกศึกษา โดยใช้เถ้าแกลบซึ่งเป็นของเสียทางการเกษตรที่มีอยู่ในปริมาณมากเป็นสารตั้งต้น ในเบื้องต้นแล้วเถ้าแกลบถูกเผาภายใต้บรรยากาศเฉื่อยที่อุณหภูมิ 600 องศาเซลเซียสเป็นเวลา 3 ชั่วโมง เพื่อผลิตเถ้าแกลบก่อน จากนั้นจึงนำเถ้าแกลบไปผ่านกระบวนการคาร์โบเทอร์มอลรีดักชันและไนไตร-เดชันที่อุณหภูมิในช่วง 1400 ถึง 1470 องศาเซลเซียส ผลิตภัณฑ์ที่ได้นั้นสามารถจำแนกออกได้เป็น 3 ส่วน ได้แก่ ผงสีเทาเข้มที่มีคาร์บอนปะปนอยู่ที่ก้นของภาชนะใส่สารตัวอย่าง ชั้นของวัสดุที่มีลักษณะเป็นเส้นใยสั้นสีขาวที่ด้านบนของสารสีเทาเข้ม และเส้นใยยาวที่ขอบของภาชนะใส่สารตัวอย่าง ผลจากการวิเคราะห์การกระเจิงของรังสีเอกซ์ ยืนยันว่าผลิตภัณฑ์ทั้งสามรูปแบบนั้นมีซิลิคอนไนไตรด์เป็นองค์ประกอบหลัก ซึ่งมีลักษณะเป็นผลึก ภาพจากกล้องจุลทรรศน์แบบส่องผ่านแสดงให้เห็นว่าเส้นใยยาวและสารสีเทาเข้มนั้นเป็นผลึกแบบโพลีคริสตัล ในขณะที่ชั้นด้านบนที่มีลักษณะเป็นเส้นใยสั้นนั้นเป็นกลุ่มของซิลิคอนไนไตรด์ที่มีลักษณะเป็นผลึกเดี่ยว จากการทำปฏิกิริยาออกซิเดชันที่อุณหภูมิเปลี่ยนแปลงของผลิตภัณฑ์สีเทาเข้มนั้น พบว่าผงสีเทาเข้มนั้นประกอบด้วยคาร์บอนที่เหลืออยู่ โดยที่สามารถกำจัดคาร์บอนนั้นออกไปได้ สัดส่วนเชิงมวลของผงสีเทาเข้มจะลดลงในขณะที่สัดส่วนเส้นใยยาวสีขาวกับชั้นเส้นใยสั้นสีขาวด้านบนจะเพิ่มขึ้นเมื่อปฏิกิริยาเกิดขึ้นที่อุณหภูมิสูงขึ้นหรือช่วงเวลาที่ยาวขึ้น จากการศึกษาโดยการเปลี่ยนอัตราการใช้ของก๊าซผสมสำหรับการทำปฏิกิริยา พบว่ากระบวนการนี้เกี่ยวข้องกับการกำเนิดไอของสารที่ประกอบด้วยซิลิคอน การศึกษาพบว่าก๊าซไฮโดรเจนเป็นสิ่งจำเป็นในการกำเนิดไอของซิลิคอนมอนอกไซด์ และการโตของเส้นใย ปฏิกิริยาของก๊าซและของแข็งระหว่างไนโตรเจน คาร์บอน และ ซิลิกาถูกทำให้ดียิ่งขึ้นในกระบวนการคาร์โบเทอร์มอลรีดักชันและไนไตรเดชันของเถ้าแกลบที่ได้จากการปรับสภาพด้วยกรดก่อน นอกจากนี้ยังได้มีการศึกษากลไกการเกิดปฏิกิริยาโดยการเปรียบเทียบกับกระบวนการคาร์โบเทอร์มอลรีดักชันและไนไตรเดชันของซิลิกาบริสุทธิ์ผสมกับคาร์บอนในปริมาณที่มากเกินไป

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สาขาวิชา.....วิศวกรรมเคมี.....ลายมือชื่ออาจารย์ที่ปรึกษา .....  
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RUTTAIRAT PRECHARYUTASIN : EFFECTS OF REACTION  
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NITRIDATION OF RICE HUSK ASH FOR SILICON NITRIDE SYNTHESIS.  
THESIS ADVISOR : VARONG PAVARAJARN, Ph.D.  
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The synthesis of silicon nitride, one of the most promising structural materials for high-temperature and high mechanical-stress applications, from rice husk, which is an abundant agricultural waste was investigated. Rice husk was first pyrolyzed at 600°C for 3 h to produce rice husk ash (RHA). The RHA was then subjected to the carbothermal reduction and nitridation process at the temperature in the range of 1400-1470°C. The product obtained could be categorized into three forms, i.e. carbon containing dark gray powder at the bottom of the sample holder, white fibrous material on top and long fibers on the edge of sample holder. X-ray diffraction analysis confirms that silicon nitride is the major crystalline constituent in all product types. Transmission electron micrographs reveal that the long fiber is polycrystalline while the fibrous top layer consists of the collection of silicon nitride single crystals. The temperature programmed oxidation of the dark gray product suggests that the dark gray powder contains residual carbon, which can be removed. Mass fraction of dark gray powder decreases, while the fraction of both white long fibers and white fibrous top layer increase when either reaction temperature or reaction duration is increased. By changing the overall flow of the gas mixture during the reaction, it is suggested that the process involves in the generation of siliceous species. Hydrogen addition is found to be essential for generation of silicon monoxide vapor and formation of fibers. Gas-solid reaction between nitrogen, carbon and silica is enhanced in the carbothermal reduction and nitridation of the acid-treated rice husk ash. Mechanism of the process is also investigated by comparing with the carbothermal reduction and nitridation of pure silica mixed with excess carbon.

Department...Chemical Engineering..... Student's signature.....  
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# CHAPTER I

## INTRODUCTION

Rice husk is an abundant agricultural waste material in Thailand. It has nutritive properties, resistance to degradation and high ash content. The major constituents of rice husk are cellulose (38%), lignin (22%), ash (20%), pentosan (18%) and other (2%) [James and Rao, 1986]. Their compositions vary with variety of crops, growth climate and geographic location [Luh, 1991]. Endeavour to use rice husks have been obstructed by their woody and sharp characteristic as well as toughness. So, current applications of rice husks are in low-value agricultural areas such as fuel, animal feed, and fertilizer. Other applications in high-value are production of organic chemical products, activated carbon production, etc. However, rice husk has been recognized as high silica-content agricultural product. Silica contained in rice husk is mainly localized in the tough interlayer of the husk and fills in the spaces between the epidermal cell [Houston, 1972; Ding, 1986; Krishnarao and Godkhindi, 1992]. After burning, rice husk ash (RHA) containing 87-97% amorphous silica with small proportion of metallic compounds is obtained [Chen and Chang, 1991]. This silica has been used to synthesize various siliceous species, such as silicon, silicon nitride, silicon carbide and magnesium silicide [Real et al., 1996]. The high price of these materials motivated the use of rice husk as an inexpensive starting material.

Silicon nitride ( $\text{Si}_3\text{N}_4$ ) is one of the most promising structural materials for high-temperature and high mechanical stress applications because of its excellent properties such as high strength retention at elevated temperature, low thermal expansion coefficient and good thermal shock resistance. It has much higher creep resistance than metals and its thermal shock resistance is much better than other ceramics. Moreover, silicon nitride is inert to many chemicals. Thus, another benefit of silicon nitride is its corrosion resistance. For these good properties, technology of silicon nitride materials has been studied intensively for more than 40 years in order to use silicon nitride instead of stainless steel or nickel-based alloy which is inferior in both properties and life-time.

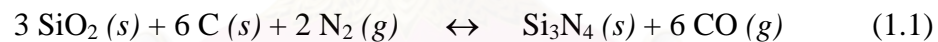
Applications of silicon nitride depend upon its high temperature strength, good thermal shock resistance and chemical inertness. Reports on the use of silicon nitride as a refractory material appeared in the early 1950s. At that time, silicon nitride was produced by either the carbothermal reduction of silica ( $\text{SiO}_2$ ) in the presence of nitrogen or by the direct nitridation of silicon. Silicon nitride has also been used as high temperature and unlubricated rollers and ball bearing for various applications, such as in oil drilling, sterilizable and unlubricated dental drills, and vacuum pumps, because of its high wear-resistance, low friction and high stiffness [Datton and Drobeck, 1986].

The development of silicon nitride ceramics as potential high-temperature structural engine materials markedly accelerated in the early 1960s. It was an outcome of a deliberate and structure search for new materials with good high-temperature properties, especially the resistance to thermal shock. This led to the development and subsequent testing of a wide range of silicon nitride components such as piston and gas turbine blade for internal combustion engine. It was also found that the low specific density of silicon nitride turbo charger could improve the engine response during acceleration, comparing to the heavier metal parts. The nozzles of certain rockets have already been prepared by using silicon nitride [Tsuruto et al., 1990]. It should be noted that these applications are not very-high-temperature applications originally envisaged, but they rely on low density (mass and inertia) of the silicon nitride components coupled with high strength and toughness required to withstand impact damaged.

In the past 30 years, during which most of the considerable developments on silicon nitride has been conducted primarily in the ceramics and electronics communities, many different aspects have been explored. Current development concerns further introduction of silicon nitride components to diesel and spark-ignited engines in the location where low mass and improved wear resistance are required. Examples of such components are exhaust valves, valve spring retainers, bucket tappets, stator blades, valve springs and rocker arm pads [Wotting et al., 1996]

Silicon nitride exists as amorphous and crystalline forms. Two common crystal structures of silicon nitride are  $\alpha$ -phase and  $\beta$ -phase, both appearing to be hexagonal [Turkdogan et al., 1958].  $\beta$ -silicon nitride is more desirable structure for high-temperature engineering applications because of its high temperature strength and excellent thermal shock resistance [Lange, 1979]. The fabrication of  $\beta$ -silicon nitride parts usually starts from  $\alpha$ -silicon nitride powder mixed with sintering additives which is subsequently sintered at high temperature. During sintering process, the transformation of  $\alpha$ -phase to  $\beta$ -phase occurs, providing desirable microstructure having high mechanical and thermal strength [Lange, 1979; Ault and Yeckley, 1994].

There are three typical processes for producing silicon nitride powder [Alcala et al., 2001]. Each process is discussed in the next section. One of the common method used process is carbothermal reduction and nitridation of silica. Because high-purity fine silica and carbon are commercially available and inexpensive. However, the product from this process has purity problem from residual carbon. The overall reaction of the carbothermal reduction and nitridation of silica is as follow [Li et al., 1991; Wang and Dai, 1996]:



The silicon nitride obtained from this process can be in the form of powder, fibers or needle-like particles. The shape of the silicon nitride particles is the result of a nucleation mechanism. Reaction (1.1) is endothermic, with the heat of reaction approximately 1,268 kJ/mol  $\text{Si}_3\text{N}_4$  at 1,427°C [Weimer et al., 1997]. Kinetically, reaction (1.1) is reported to be slow, requiring many hours to complete. Moreover, this process requires high reactivity and good distribution of raw materials, i.e. silica and carbon, to achieve satisfactory extent of the reaction.

As previously described, rice husk ash naturally contains both silica and carbon which are well mixed with each other. Therefore, it is considered to be a good candidate for the carbothermal reduction and nitridation process. Furthermore, it is economical to produce high-valued silicon nitride from low-valued agricultural waste. The potential to produce silicon nitride from rice husk has been recognized for more

than 20 years, but it has not yet been industrialized. The main reason is that silicon nitride obtained is usually accompanied by other by-products, such as silicon carbide or silica. In general, silicon nitride powder can be prepared from RHA at temperature in the range of 1260 and 1500°C under a flow of nitrogen. The reaction takes place at temperature relatively lower than the conventional SiO<sub>2</sub>/C mixture, while the nitridation rate is distinctively faster. It has been reported that the rate of the reaction depends upon the treatment of rice husk before the carbothermal process as well [Real et al., 1996].

This work is intended to find appropriate conditions for producing silicon nitride from rice husk ash via the carbothermal reduction and nitridation process. The main purpose of this research is to investigate effects of various parameters on the extent of the reaction, as well as the characteristic of the product. The scopes of this study are as following:

1. For the preparation of rice husk ash, rice husk is heated to 600°C, at the rate of 10°C/min, under the continuous flow of argon for 3 hours. The flow rate of argon was fixed at 36 l/h (measured at room temperature).

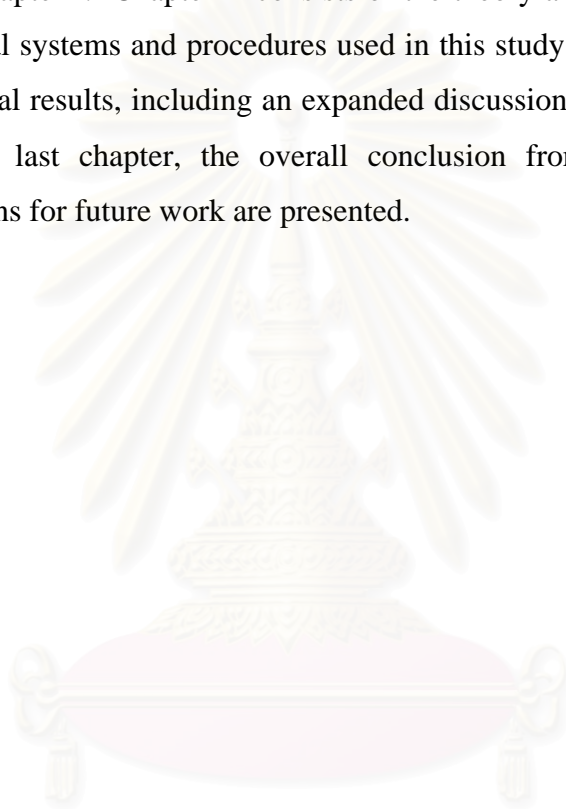
2. Silicon nitride is synthesized via the carbothermal reduction and nitridation of RHA. The parameters of the reaction investigated include reaction temperature, flow rate of reactant gas mixture, reaction duration, composition of reactant gas mixture and the pretreatment of rice husk. The reaction temperatures investigated are 1400, 1450 and 1470°C, respectively. The overall flow rate of the gas mixture is in the range of 30-80 l/h. The reaction time investigated is 3 to 10 h. The reaction gas is consisted of nitrogen and hydrogen, whereas the concentration of hydrogen is in the range of 0 to 40 %. The rice husk is pretreated by either washing with distilled water or hydrochloric acid (HCl).

3. The silicon nitride products are characterized by using powder X-ray diffraction (XRD) for crystalline phase analysis. The functional group in the samples is determined by using an Infrared Spectrometer (IR). The carbon contents and thermal behaviors of the samples are performed on a Thermogravimetric Analysis



(TGA). Product morphology is verified by Scanning Electron Microscopy (SEM). The morphology and crystallographic imaging of the samples are also observed by Transmission Electron microscope (TEM).

This 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 presented in Chapter I. Chapter II consists of the theory and literature survey, while the experimental systems and procedures used in this study are shown in Chapter III. The experimental results, including an expanded discussion, are given in Chapter IV. Finally, in the last chapter, the overall conclusion from the results and some recommendations for future work are presented.



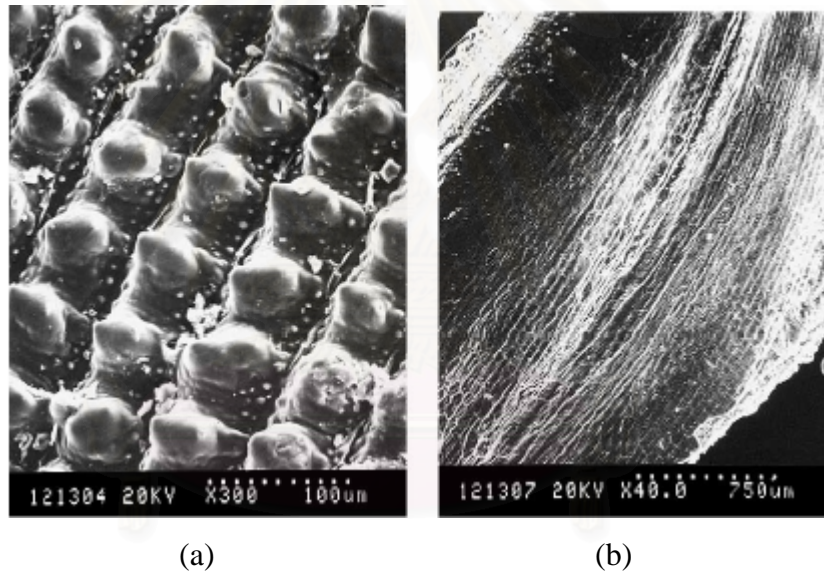
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## CHAPTER II

### THEORY AND LITERATURE SURVEY

#### 2.1 Properties of Rice Husk

The compositions of rice husk are cellulose, lignin, small quantities of proteins and vitamins, inorganic compounds rich in silicon and small concentration of other metals [Mehta, 1996]. The quantity of each composition depends on the soil type, plant variety and climatic conditions, etc. Figure 2.1 shows SEM micrographs of rice husk [Liou, 2004].



**Figure 2.1** Scanning electron micrographs of rice husk: (a) outer epidermis of rice husk; (b) inner epidermis of rice husk

Figure 2.1a shows the outer epidermis of rice husk, which has corrugated structure, while Figure 2.1b shows its inner epidermis. The outer surface of rice husk was highly ridged, and the ridged structures had a linear profile. Silica is mainly localized in the tough interlayer of the rice husk and also filling in the space between the epidermal cells [Sharma et al., 1984; Krishnarao and Godkhindi, 1992]. The physical and chemical properties analysis data of rice husk are shown in Table 2.1 [Fang et al., 2004].

**Table 2.1** Rice husk analysis data

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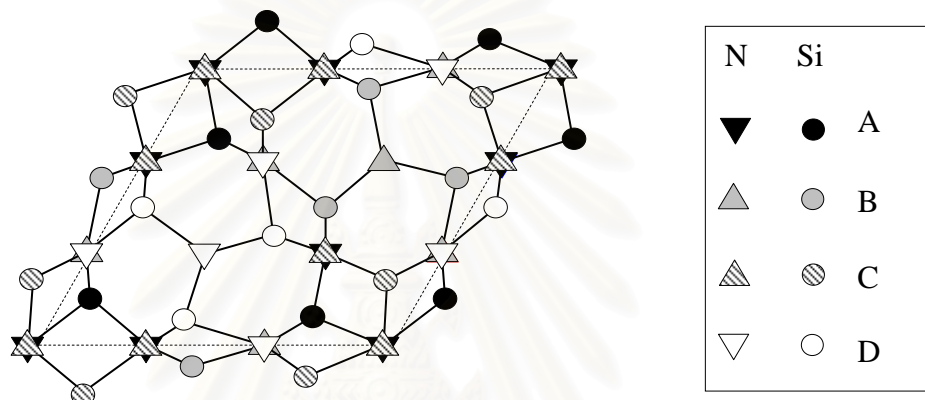
<b>Proximate Analysis</b>	% by mass
Moisture	6%
Ash	16.92%
Volatile	51.98%
Fixed carbon	25.10%
<b>Ultimate Analysis</b>	
Carbon	37.60%
Hydrogen	4.89%
Sulphur	0.01%
Nitrogen	1.89%
Oxygen	32.61%
Ash	16.92%
Gross Calorific Value	13.4 MJ/kg
<b>Physical Properties</b>	
Diameter range	0-10 mm
Equivalent mean diameter	1.60 mm
Natural packing density	122 kg/m <sup>3</sup>
Real density	500 kg/m <sup>3</sup>

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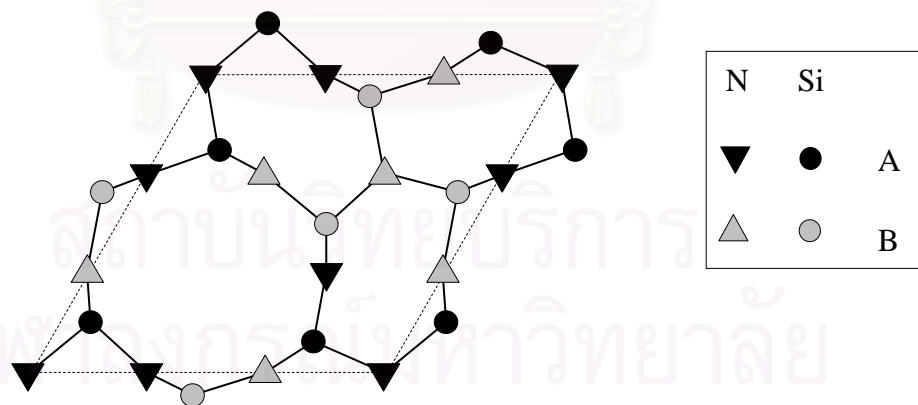
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## 2.2 Crystal Structure of Silicon Nitride

It has been generally accepted that there are two common forms of crystalline silicon nitride, designated as  $\alpha$ - and  $\beta$ -forms, respectively. Detailed X-ray diffractometry (XRD) examination in the mid-1950s have proved that the crystal structure of both  $\alpha$  and  $\beta$  polymorphs are hexagonal [Turkdogan et al., 1958]. However, their respective structural dimensions are different. The structures of  $\alpha$ -phase and  $\beta$ -phase are shown in Figure 2.2 and Figure 2.3 respectively.



**Figure 2.2**  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> unit cell: the structure of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> can be described as a stacking of Si-N layers in ...ABCDABCD... sequence.



**Figure 2.3**  $\beta$ -Si<sub>3</sub>N<sub>4</sub> unit cell: the structure of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> can be described as a stacking of Si-N layers in ...ABAB... sequence.

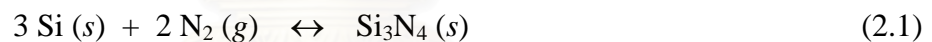
## 2.3 Commercial Techniques for Mass-Producing Silicon Nitride Powder

Silicon nitride is not found in nature, but can be synthesized by a number of different techniques. Pure silicon nitride is difficult to produce as a fully dense material. For industrial production of silicon nitride powder, silicon, silica (SiO<sub>2</sub>) and silicon tetrachloride (SiCl<sub>4</sub>) are the three commonly used starting materials because they are available in high purity on an economic basis or can be easily purified.

Silicon nitride powders are mainly produced in commercial scale by three methods: direct nitridation of silicon, high-temperature decomposition of silicon diimide and carbothermal reduction and nitridation of silica [Alcala et al., 2001].

### 2.3.1 Direct Nitridation of Silicon

This process is based on contacting elemental silicon with nitrogen at temperature in the range of 1200-1400°C. Although the true mechanism is unknown, the overall reaction of this process can be represented by the following equation:

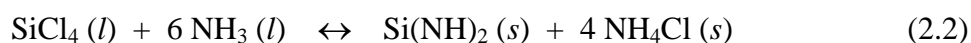


The reaction is highly exothermic. Extreme care must be taken to prevent temperature run-away, which results in melting of silicon particles. The direct nitridation process is more complicated than Equation (2.1) implies. Several models have been proposed to describe the nitridation of silicon [Atkinson et al., 1973; Jennings, 1983; Varma et al., 1991; Pigeon and Varma, 1993], but there is no general agreement regarding the mechanism of the nitridation.

The production cost for this process is low, compared to other processes mentioned earlier, since the process is one simple step using inexpensive reactants. However, the quality of product obtained is low. This process is an inexpensive option for the applications in which metal impurities, originating from silicon, contained in the product silicon nitride can be tolerated.

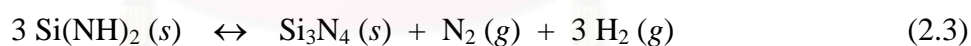
### 2.3.2 High-Temperature Decomposition of Silicon Diimide

This process could be described as a two-step process. The first step is the liquid phase reaction between silicon tetrachloride and ammonia at room temperature, as follows:



In principle, the liquid phase reaction of silicon tetrachloride with ammonia can be performed in three different ways: (a) liquid  $\text{SiCl}_4$  with liquid  $\text{NH}_3$ , (b) gaseous  $\text{SiCl}_4$  with liquid  $\text{NH}_3$  and (c) liquid  $\text{SiCl}_4$  and gaseous  $\text{NH}_3$ . In all three cases, fine silicon diimide and ammonium chloride particles are formed. The ammonium chloride can be removed by series of washing with liquid ammonia.

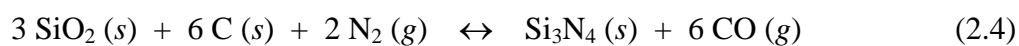
After removing the ammonium chloride, the silicon diimide is given a polymerization via heat treatment in nitrogen or ammonia [Yamada, 1993]. The polymer is then pyrolyzed at  $1100^\circ\text{C}$  in nitrogen to produce amorphous silicon nitride. Subsequent heat treatment at temperature higher than  $1430^\circ\text{C}$  initiates conversion of amorphous product into  $\alpha$ -crystalline form, which may be represented by an overall stoichiometric equation as:



Since reactants are liquids or gases, very pure silicon nitride with a high content of  $\alpha$ -form ( $> 95\%$ ) can be prepared [Ault and Yeckley, 1994]. However, the production cost is high due to complexities of the process and extensive efforts to purify the intermediate silicon diimide.

### 2.3.3 Carbothermal Reduction and Nitridation of Silica

The carbothermal reduction of silica powder under nitrogen was the earliest method used for silicon nitride production [Riley, 2000]. It produces silicon nitride according to the following overall reaction [Segal, 1985]:



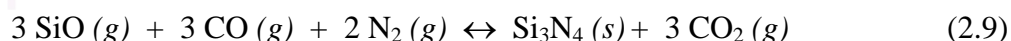
This reaction also occurs via a gas-solid mechanism. The mechanism of reaction (2.4) is believed to involve multiple steps, where silicon monoxide acts as an intermediate [Arik, 2003]. It is proposed that silicon monoxide is produced by reduction of silica by either carbon or carbon monoxide.



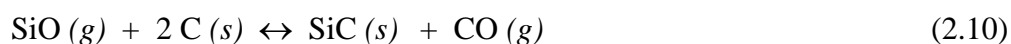
Carbon dioxide generated from reaction (2.6) can further react with carbon to produce more carbon monoxide :



Silicon nitride is then produced by reaction of silicon monoxide, nitrogen gas and either solid carbon or carbon monoxide according to reaction (2.8) for heterogeneous nucleation, but growth is believed to occur by a gas phase process according to reaction (2.9) [Weimer et al., 1997].



The problem of this method is associated with the formation of silicon carbide, because silicon carbide is produced by reaction of silicon monoxide with carbon.



Furthermore, silicon nitride can be converted to silicon carbide in the presence of carbon as well, according to reaction (2.11):



Therefore, the reaction conditions are particularly important in establishing which compound will be formed.

The carbothermal reduction and nitridation synthesis of  $\alpha$ -silicon nitride is controlled by the nucleation of  $\alpha$ -silicon nitride crystallites. The formation of  $\alpha$ -silicon nitride nuclei occurs through a fine amorphous Si-O-C intermediate [Weimer et al., 1997]. Fine  $\alpha$ -silicon nitride powder can be produced directly by using very fine silica. Kinetically, overall reaction is reported to be slow, requiring many hours (up to 12 hours) to complete. The reaction (2.4) is usually performed at temperature in the range of 1200-1450°C, depending on the reactivity of raw materials. If the carbothermal reduction process follows Eqs 2.5 to 2.9, physical contact between carbon and silica is essential for SiO vapor formation. Full conversion using a stoichiometric ratio of SiO<sub>2</sub>:C (1:2) can occur only if there is perfect contact between carbon and silica particles. Hence, an excess amount of carbon is required for full transformation of silica to silicon nitride, and free carbon can remain in silicon nitride powder. Although the remaining carbon can be removed by heat treatment in air, the silicon nitride would be oxidized as well. Consequently, the powder synthesized by this method often suffers from purity problem associated with residual carbon and oxygen content.



## 2.4 Preparation of Rice Husk Ash

Rice husk has high contents of high reactivity silica. So, new way to prepare high-purity silica from rice husks has been intensively investigated. Many researchers have studied methods for the production of pure silica from rice husk ash (RHA), such as acid leaching, gasification, alkaline extraction and pyrolysis [Hanafi et al., 1980; Amick, 1982; Hunt et al., 1984; James and Rao, 1985; Chakraverty et al., 1988; Chakraverty and Kaleemullah, 1991; Real et al., 1996; Kalapathy et al., 2000]. RHA obtained from pyrolysis of rice husk at temperature below 700°C consists of amorphous silica, carbon and metallic impurities. James and Rao (1986) studied about silica in rice husk ash and concluded that the physical characteristics and the chemical reactivity of amorphous silica in rice husk ash depend on temperature and soaking time. Published data show that the amount of silica and carbon presented in pyrolyzed rice husk are approximately 48% and 50% by mass, respectively. When RHA is produced by uncontrolled pyrolysis, the ash is generally crystalline and presents poor properties. However, by pyrolysis under controlled temperature and atmosphere, a highly reactive RHA can be obtained.

Many researchers have studied the effects of various rice husk pretreatment methods, such as washing by distilled water and acid treatment, on the properties of RHA [Amick, 1982; Hunt et al., 1984; James and Rao, 1985; Chakraverty et al., 1988; Real et al., 1996]. It was found that pretreatment of rice husks with acid solution was effective in removing most of the metallic impurities, as well as, producing silica ash with high specific surface area [Hanafi et al., 1980; Ibrahim et al., 1980; Della et al., 2002]. Moreover, the pyrolysis temperature could be decreased for acid treated rice husks [Chakraverty et al., 1985; Sugita et al., 2004]. Chemical compositions and physical properties of RHA and pyrolyzed ash from hydrochloric acid-treated rice husk (ATRH) are shown in Table 2.2 [Sugita et al., 2004]. With hydrochloric acid pretreatment, the pozzolanic activity of RHA is stabilized and enhanced, while the sensitivity of the pozzolanic activity of the RHA to the burning condition is reduced [Sugita et al., 2004]. Further studies on the effects of rice husk pretreatment and pyrolysis temperature on amount of amorphous silica in RHA have also been investigated. It was found that amorphous silica obtained by pyrolysing the rice husks, which was leached in hydrochloric acid, at 600°C contained the highest amount of

amorphous silica [Real et al., 1996; Yalcin and Sevinc, 2001; Fang et al., 2004; Sugita et al., 2004]. Table 2.3 shows amount of amorphous silica in the RHA and ATRH pyrolyzed at different temperatures [Sugita et al., 2004].

**Table 2.2** The chemical composition and physical properties of RHA and ATRH

	RHA	ATRH
Loss on ignition (%)	2.31	2.65
SiO <sub>2</sub> (%)	92.40	96
Al <sub>2</sub> O <sub>3</sub> (%)	0.30	0.1
Fe <sub>2</sub> O <sub>3</sub> (%)	0.40	0.2
CaO (%)	0.70	0.2
MgO (%)	0.30	0.1
Na <sub>2</sub> O (%)	0.07	0.03
K <sub>2</sub> O (%)	2.54	0.16
P <sub>2</sub> O <sub>5</sub> (%)	0.51	0.18
MnO (%)	0.11	0.02
Cl (%)	0.11	0.01
Specific Gravity (g/cm <sup>3</sup> )	2.10	2.12
Nitrogen Adsorption (m <sup>2</sup> /g)	110	311

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**Table 2.3** Amount of silica<sup>a</sup> in RHA and ATRH

Sample	Pyrolysis Temperature (°C)	Amount of amorphous silica (%)
RHA	550	88.6
	600	89.6
	700	75.4
	800	40.2
ATRH	550	94.8
	600	95.1
	700	95
	800	95.7

<sup>a</sup>Determined by glycerol method [Paya et al., 2001]

## 2.5 Synthesis of Silicon Nitride from Rice Husk Ash

The silicon nitride can be in the form of powder, fibers or a needle-like shape. The shape of the silicon nitride particles is the result of nucleation mechanism. Many raw materials have been used for producing silicon nitride, such as diatomite [Arik, 2003] and rice husk ash [Cutler, 1974; Hanna et al., 1985; Rahman and Riley, 1989; Kuskonmaz et al., 1996; Real et al., 2004]. The production of silicon nitride from RHA was first reported in the U.S. patent [Cutler, 1974]. It employed the carbothermal reduction and nitridation process, where the reaction temperature used was within the range of 1100-1350°C [Cutler, 1974]. Extensive studies have also been conducted to control the properties of RHA to suit the silicon nitride production. Nevertheless, silicon nitride obtained from the carbothermal reduction of RHA is usually accompanied by silicon carbide (SiC) and other metallic impurities. Barnitskaya et al. (1983) have suggested that pure silicon nitride can only be formed if small amount of Fe is added to the raw materials, whereas Siddiqi and Hendry (1985) have showed that Fe promotes silicon carbide formation over silicon nitride. As the result, many on researchers emphasize the production of silicon nitride and silicon carbide composites instead. It has been reported that the carbothermal reduction and nitridation at temperature in the range of 1450-1500°C for 6 h under nitrogen flow results in the silicon nitride and silicon carbide composites [Yamaguchi, 1986; Kuskonmaz et al., 1996]. For the synthesis of pure silicon nitride, effective removal of impurities before the reaction and controlling of the reaction conditions are very important. In general, silicon nitride powders can be prepared from RHA at temperature between 1260 and 1500°C under nitrogen atmosphere. The reaction temperature is relatively lower than when the conventional SiO<sub>2</sub>/C mixture is used as starting materials. The nitridation rate of the pyrolyzed RHA is also distinctively faster than that of the SiO<sub>2</sub>/C mixture [Hanna et al., 1985; Liou and Chang, 1996]. It has been reported in the study of the carbothermal reduction of rice husks by simultaneously controlling both reaction rate and the concentration of CO generated in the system that silicon nitride obtained depends upon the CO concentration [Real et al., 2004]. The excess carbon is necessary component in the carbothermal reduction for production of silicon nitride because a full conversion at the stoichiometric coefficient can only be realized in the case of a full contact between the carbon and

the silica particles, which is unlikely to occur under actual reaction conditions [Kuskonmaz et al., 1996].

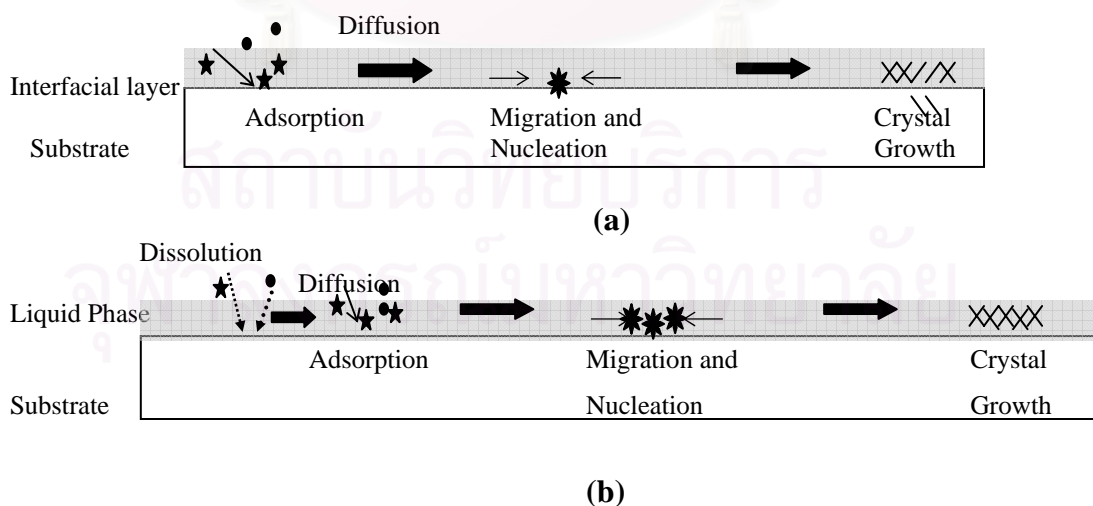
One of the key factors that significantly affect the extent of the nitridation reaction is the presence of hydrogen in the reactant gas mixture. Rahman and Riley (1989) prepared silicon nitride powder by nitriding the pyrolyzed RHA under 95% nitrogen and 5% hydrogen. They found that hydrogen addition was beneficial in accelerating the rate of nitride formation. Although exact role of hydrogen is still unclear, an addition of hydrogen to the nitridation atmosphere has long been known to increase the overall rate of the nitridation of silicon, especially at lower temperatures [Parr et al., 1961; Popper and Ruddlesden, 1961; Rahaman and Moulson, 1984; Barsoum et al., 1991]. The nitridation with pure nitrogen usually requires very long reaction time (more than 10 hours), and the conversion is low. By addition hydrogen to the reactance gas, high conversion is usually achieved within a short period of reaction time [Dervišbegovic and Riley, 1981; Rahaman and Moulson, 1984]. Ekelund (1990) found that the carbothermal reduction and nitridation rate is not enhanced by an increase in nitrogen pressure.

There are some potential chemical reactions suggested in the literature that it is possible to get nano phase silicon nitride via vapor-phase reactions involving silicon monoxide, SiO. It is believed that, in the carbothermal reduction and nitridation of silica, SiO plays an important role in the formation of silicon nitride [Zhang and Cannon, 1984; Durham et al., 1988; Durham et al., 1991; Mizuhara et al., 1991]. It is also suspected that SiO generated from surface oxides is involved in the formation of silicon nitride [Barsoum et al., 1989; Barsoum et al., 1991; Pigeon et al., 1993]. However, the intrinsic role of SiO in the process of silicon nitride formation still remains unclear.

The silicon nitride powders from RHA usually are not as fine as that obtained from SiO<sub>2</sub>/C mixture. It is therefore an objective of this work to investigate the effects of reaction parameters on the carbothermal reduction and nitridation of RHA for silicon nitride synthesis.

## 2.6 Mechanisms for Crystal Growth from Gas Phase

Two types of mechanism are often used to explain the crystal growth associated with gas phase, as shown in Figure 2.4 [Kawai and Yamakawa, 1998]. In the vapor-solid (VS) mechanism, Fig. 2.4(a), chemical species diffuse toward a substrate through an interfacial gas layer, and adsorbed on the surface of the substrate. The adsorbed species may be mobile on the surface. Subsequently, nucleation and crystal growth occur, accompanied by the elimination of any by-product. In VS mechanism, the diffusion of the chemical species in the gas phase and surface migration of them on the substrate are fast. Therefore, high deposition rate will be obtained if a reaction between the chemical species is fast enough. On the other hand, there are few studies focusing on the use of the vapor-liquid-solid (VLS) mechanism. As shown in Fig. 2.4(b), if liquid-phase exists on a substrate, chemical species must be first dissolved in the liquid phase for crystal growth. Next, they diffuse in liquid and adsorbed on the substrate. Finally, crystal growth occurs via nucleation in the liquid phase. The diffusion rates of the chemical species in the liquid phase are probably much slower than in gas phase. Therefore, the rate of the supplement of chemical species to nucleus for crystal growth is very small. This results in high nucleation density and the formation of the finer crystals than those through the VS mechanism.



**Figure 2.4** Mechanism of two types of gas phase process: (a) VS mechanism, (b) VLS mechanism.

## CHAPTER III

### EXPERIMENTAL

This chapter describes the experimental systems and procedures used in this study. The chapter is divided into four sections. Section 3.1 is raw material preparation. The synthesis of rice husk ash and silicon nitride powder are explained in the section 3.2 and 3.3, respectively. Characterizations of the products are presented in the last section.

#### 3.1 Raw Material Preparation

Rice husk used in this work was obtained from Nakorn Ratchasima province in Thailand. For normal runs, rice husk was washed and soaked in distilled water at 90°C for 3 hours to remove its impurities. Then, it was dried in an oven at 110°C for 24 hours to ensure the elimination of all possibly remaining moisture.

In some runs, where the effect of acid treatment was investigated rice husk was treated by resting in 1 M hydrochloric acid at room temperature for 1 hour. After that, it was washed and soaked in distilled water at 90°C for 3 hours to remove its impurities. Then, it was dried in an oven at 110°C for 24 hours to ensure the elimination of all possibly remaining moisture.

#### 3.2 Synthesis of Rice Husk Ash

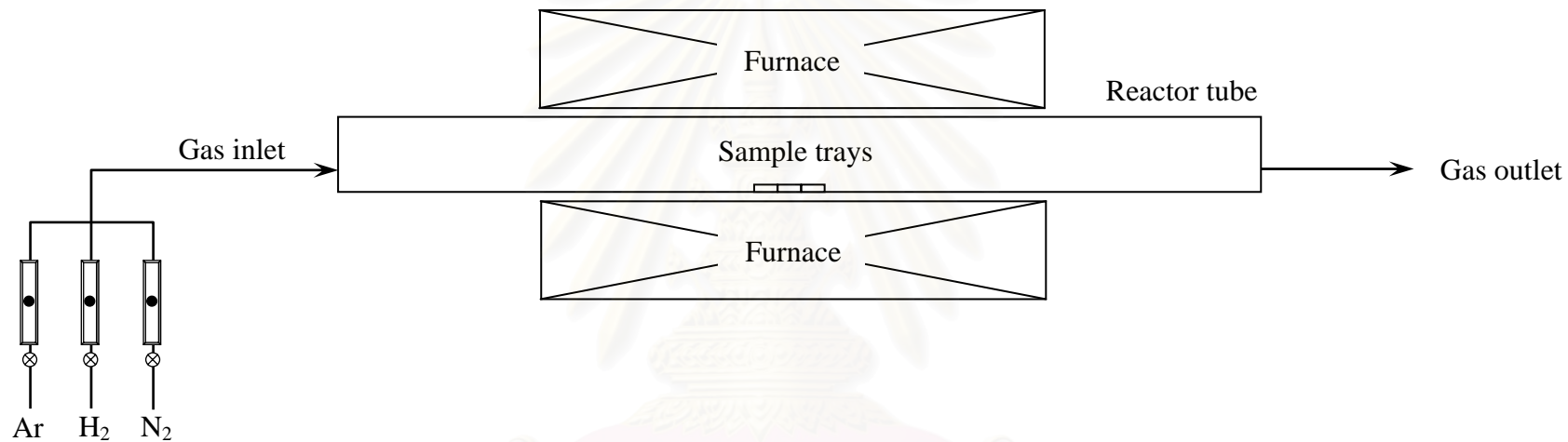
Rice husk ash was prepared from rice husk by pyrolysis. The procedures were performed in a horizontal tubular flow reactor which is an alumina tube (49 mm inside diameter × 1.2 m long) placed inside a high temperature furnace (Carbolite-STF 15/--/180). The schematic diagram of the reactor system is shown in Figure 3.1

For each run, about 2 g of rice husk was put into an alumina combustion boat (150 mm × 10 mm × 10 mm deep). Then, two boats were placed side-by-side in the uniform temperature zone of the reactor. Samples were then heated to a predetermined temperature, 600°C, at the rate of 10°C/min, under continuous flow of argon. The flow rate of argon was fixed at 36 l/h (measured at room temperature). The operation was performed under atmospheric pressure. The pyrolysis of rice husk was done for 3 hours. This condition has been reported to result in rice husk ash containing high amount of amorphous silica [Real et al., 1996; Yalcin and Sevinc, 2001; Fang et al., 2004; Sugita et al., 2004].



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**Figure 3.1** Schematic diagram of the tubular flow reactor system

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### 3.3 Synthesis of Silicon Nitride Powders

As mentioned earlier, silicon nitride was synthesized via the carbothermal reduction and nitridation process. For each run, RHA about 0.2 g was put into alumina trays (25 mm × 15 mm × 5 mm deep). The thickness of RHA layer in each tray was about 2 mm. Then, two alumina trays were placed in the uniform temperature zone of the horizontal tubular flow reactor (Figure 3.1). The reactor was purged with argon and heated up to desired temperature at constant heating rate of 10°C/min. The reaction temperatures investigated were 1400, 1450 and 1470°C, respectively. The overall flow rate of the gas mixture, i.e., nitrogen mixed with hydrogen, was in the range of 30-70 l/h (measured at room temperature). The reaction time was held at constant temperature for 3 to 10 h. The composition of hydrogen in the gas mixture investigated was varied in the range of 0-40 %. For comparison, the carbothermal reduction and nitridation of amorphous silica mixed with excess carbon (50%) under the same conditions was also investigated.

### 3.4 Characterization of the Products

The obtained products were characterized by using various techniques, as following:

#### 3.4.1 X-ray Diffraction Analysis (XRD)

Crystalline phases of the product were determined from X-ray diffraction analysis, using a SIEMENS D5000 diffractometers with  $\text{CuK}\alpha$  radiation. Each sample was scanned in the range of  $2\theta = 10\text{-}50^\circ$  with a step size of  $2\theta = 0.02^\circ$ .

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

The functional groups in the samples were determined by using a Nicolet Impact 400 infrared spectrometer. The sample was mixed with KBr and formed into a thin pellet, before measurement.

### 3.4.3 Thermogravimetric Analysis and Differential Thermal Analysis (TG/DTA)

The residual carbon content and thermal behaviors of the samples were determined by using TG/DTA analysis on a Diamond TG/DTA thermogravimetric instrument. The analysis was performed at a heating rate of 20°C/min in 200 ml/min flow of oxygen.

### 3.4.4 Scanning Electron Microscopy (SEM)

The morphology of rice husk ash as well as silicon nitride powder synthesized was examined by using a scanning electron microscope (JSM-6400, JEOL Co., Ltd.) at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

### 3.4.5 Transmission Electron Microscope (TEM)

The morphology of an individual grains in the samples was observed on a JEOL JEM-2010 Analytical Transmission Electron Microscope, operated at 80-200 keV at National Metal and Materials Technology Center (MTEC), Thailand. The crystallographic information was also obtained from the selected area electron diffraction (SAED) analysis performed in the same instrument.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Preliminary Experiments

In preliminary experiments, rice husk ash (RHA) obtained from the “Power Station of Thai Power Supply Limited.” was subjected to the carbothermal reduction and nitridation process at 1400°C for 3 h. This RHA was the result from uncontrolled burning of rice husk in the power plant. Chemical composition of this RHA is shown in Table 4.1. The nitridation results showed that this kind of RHA could not be used for the synthesis of silicon nitride, because silica in cristobalite phase was generated during the burning under uncontrolled temperature and atmosphere. X-ray diffraction analysis of the resulting product is shown in Figure 4.1. It has been generally recognized that cristobalite is the most chemically stable form of silica. Therefore, for silicon nitride synthesis from RHA, the preparation of RHA is one of the critical factor.

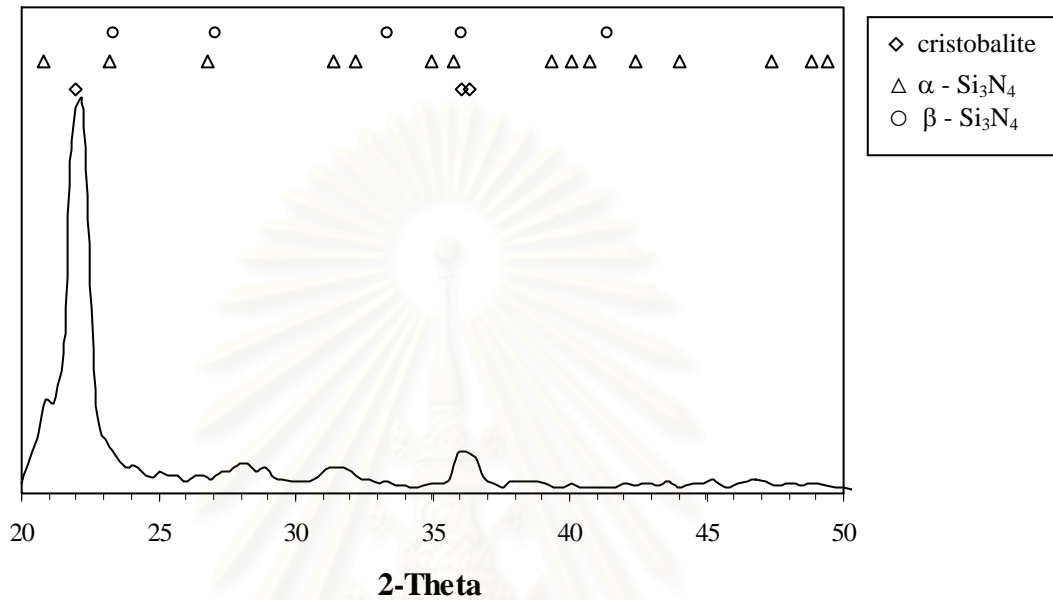
**Table 4.1** Chemical composition\* of RHA from the “Power Station of Thai Power Supply Limited.”.

Item	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub>
%	84.42	0.24	0.45	0.28	0.08	2.37	0.15	0.21

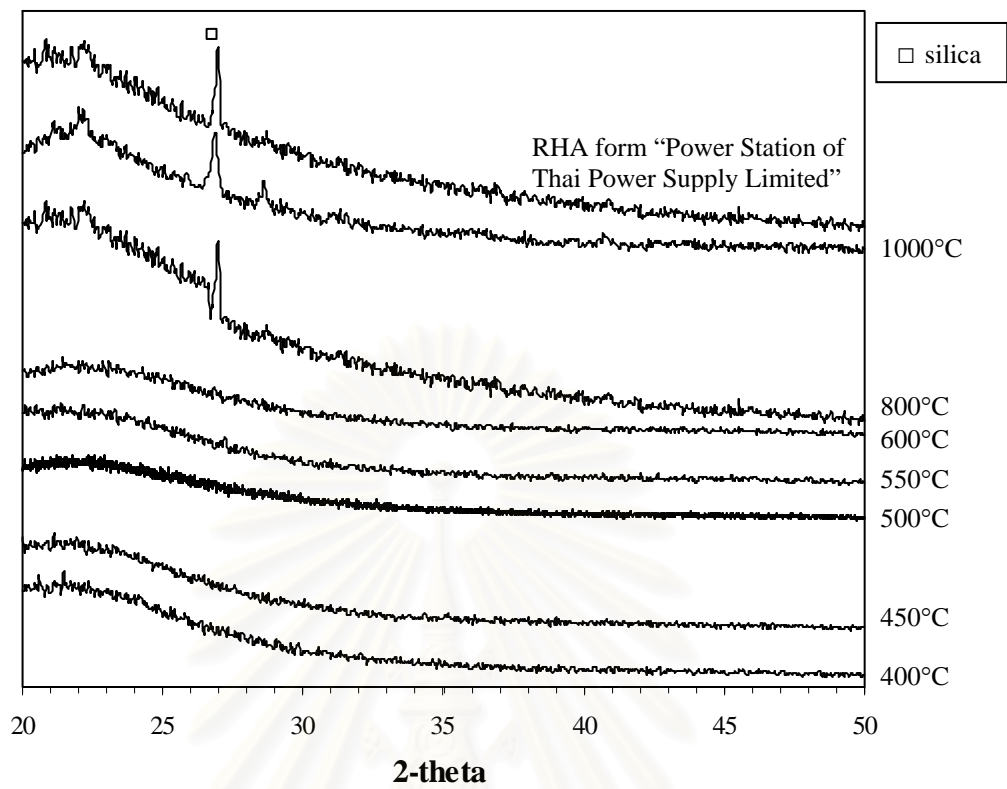
\* Test by Chemical Division, Electricity Generating Authority of Thailand

When RHA were produced by pyrolysis at temperature higher than 800°C, the RHA were generally crystalline silica. X-ray diffraction analysis of RHA from pyrolysis in each temperature under argon (flow rate of 10 ml/sec) is shown in Figure 4.2.

In this study, condition of pyrolysis is 600°C for 3 hours under argon (flow rate of 10 ml/sec) because this condition has been reported to result in the highest amount of amorphous silica [Real et al., 1996; Yalcin and Sevinc, 2001; Fang et al., 2004].



**Figure 4.1** XRD patterns of product from RHA of Power Station of Thai Power Supply Limited after the carbothermal reduction and nitridation.



**Figure 4.2** XRD patterns of RHA synthesized at various pyrolysis temperatures.

The preliminary experiments also confirmed the early report in literatures that silicon nitride synthesis via the carbothermal reduction and nitridation of RHA is unfavored at temperature lower than 1400°C. At the reaction temperature of 1300°C, no change in sample mass was detected and no silicon nitride was found. It is common believe that silica will not be reduced at this temperature [Zhang and Cannon, 1984; Jong et al., 1992]. Furthermore, it was found from the preliminary experiments that the present of hydrogen in reaction gas is nessesary for the nitridation. The product from the nitridation under pure N<sub>2</sub> atmosphere was silica in cristobalite phase with no silicon nitride. Rahman and Riley (1989) also found that hydrogen addition was beneficial in accelerating the rate of nitride formation. Therefore, according to the preliminary experiments, the standard operating condition for the nitridation in this work was chosen to be the 6h-reaction at 1450°C under flow of nitrogen mixed with 10% hydrogen at the rate of 50 l/h.

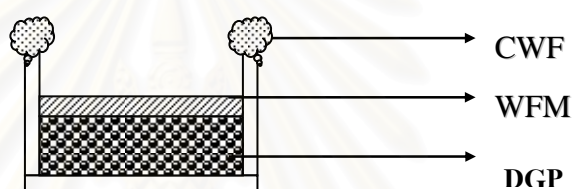
The main purpose of this study is to investigate the effects of reaction parameters on the carbothermal reduction and nitridation of rice husk ash for silicon nitride synthesis.



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#### 4.2 General Observations for the Carbothermal Reduction and Nitridation of Rice Husk Ash

This section describes general characteristic of products from the carbothermal reduction and nitridation of rice husk ash. It was observed that the products of the reaction can be classified into three portions, i.e. a layer consisted of dark gray powder at the bottom of the sample holder (hereafter referred to as DGP layer), a layer of white fibrous material on top of the dark gray layer (referred to as WFM layer) and cotton-like white fibers on the edge of sample holder (referred to as CWF layer). Figure 4.3 shows a schematic diagram, in cross-section view, of each portion of products generally obtained.



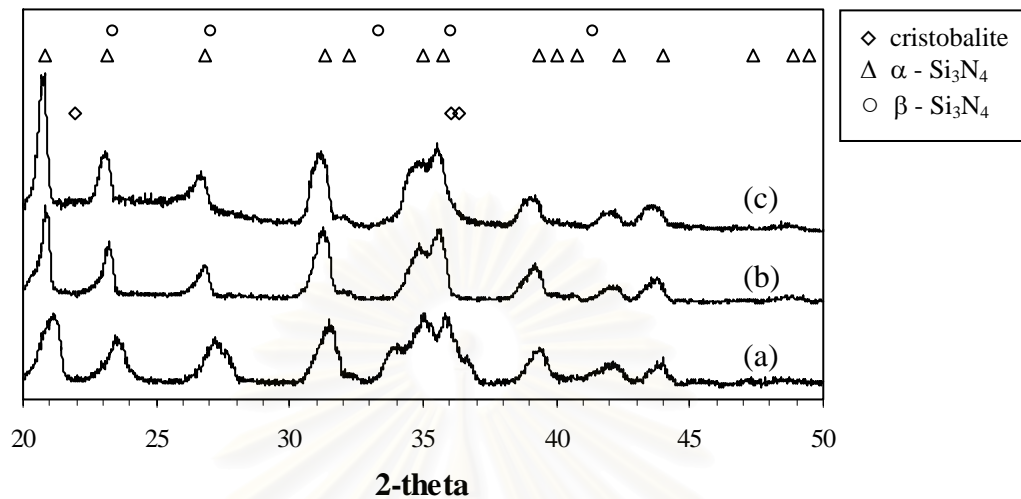
**Figure 4.3** The schematic diagram of each portion of nitridation products.

Since silicon nitride is white or light gray while RHA is black, it was anticipated that the dark gray powder in the DGP layer contained mainly residual carbon. It should be noted that both DGP and WFM layers were contained within sample holder where RHA was originally placed. On the contrary, the CWF layer was discovered outside the cavity of sample holder. All layers could be easily separated from each other.

The XRD and IR patterns of product in each portion as shown in Figure 4.4 and Figure 4.5 respectively, confirm that silicon nitride is the major crystalline phase in all product types. No other apparent crystalline phase was detected. However, since the XRD peaks are broad, the peak around  $2\theta$  of  $34.92^\circ$  and  $35.68^\circ$  are overlapped. Therefore, it is inconclusive whether there is small amount of silicon carbide in the product, because the main reflection peak of silicon carbide ( $2\theta$  of around  $35.75^\circ$ ) might be overlapped. It should be noted that silicon nitride in both DGP and WFM

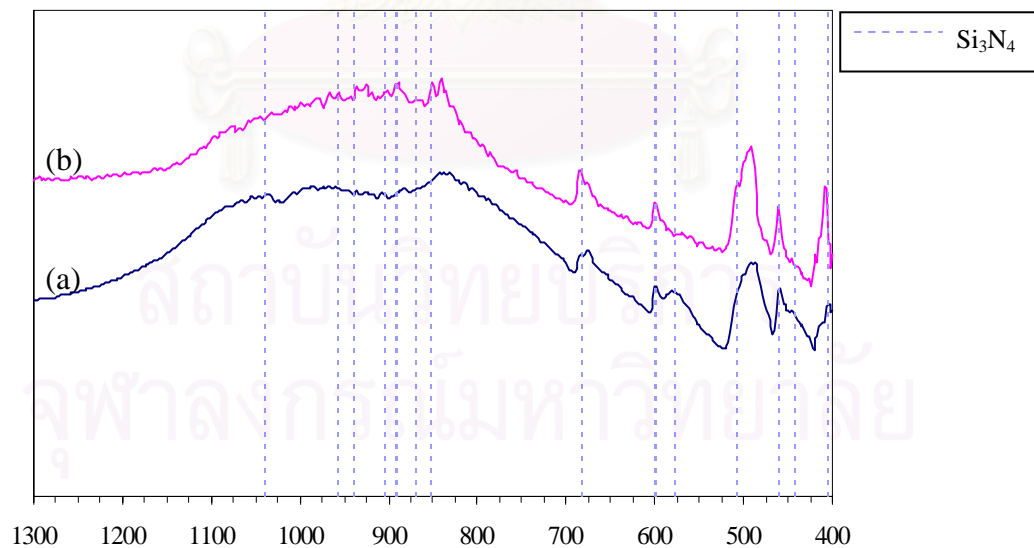


layer are  $\alpha$ - $\text{Si}_3\text{N}_4$  with no trace of  $\beta$ - $\text{Si}_3\text{N}_4$ . On the contrary, the XRD peak of CWF portion reveals the present of  $\beta$ - $\text{Si}_3\text{N}_4$  in addition to  $\alpha$ - $\text{Si}_3\text{N}_4$ .



**Figure 4.4** XRD patterns of products from the carbothermal reduction and nitridation at  $1450^\circ\text{C}$  for 6 h:

- (a) cotton-like white fibers on the edge of sample holder (CWF)
- (b) white fibrous top layer (WFM)
- (c) dark gray powder (DGP)



**Figure 4.5** IR patterns of product from the carbothermal reduction and nitridation at  $1450^\circ\text{C}$  for 6 h:

- (a) cotton-like white fibers on the edge of sample holder (CWF)
- (b) white fibrous top layer (WFM)

Characterization of the product obtained was also conducted by X-ray Photoelectron Spectroscopy (XPS). The results, shown in Table 4.2 confirm that all product types contain silicon, nitrogen and oxygen.

**Table 4.2** Elemental composition of product obtaining from the X-ray Photoelectron Spectroscopy (XPS)

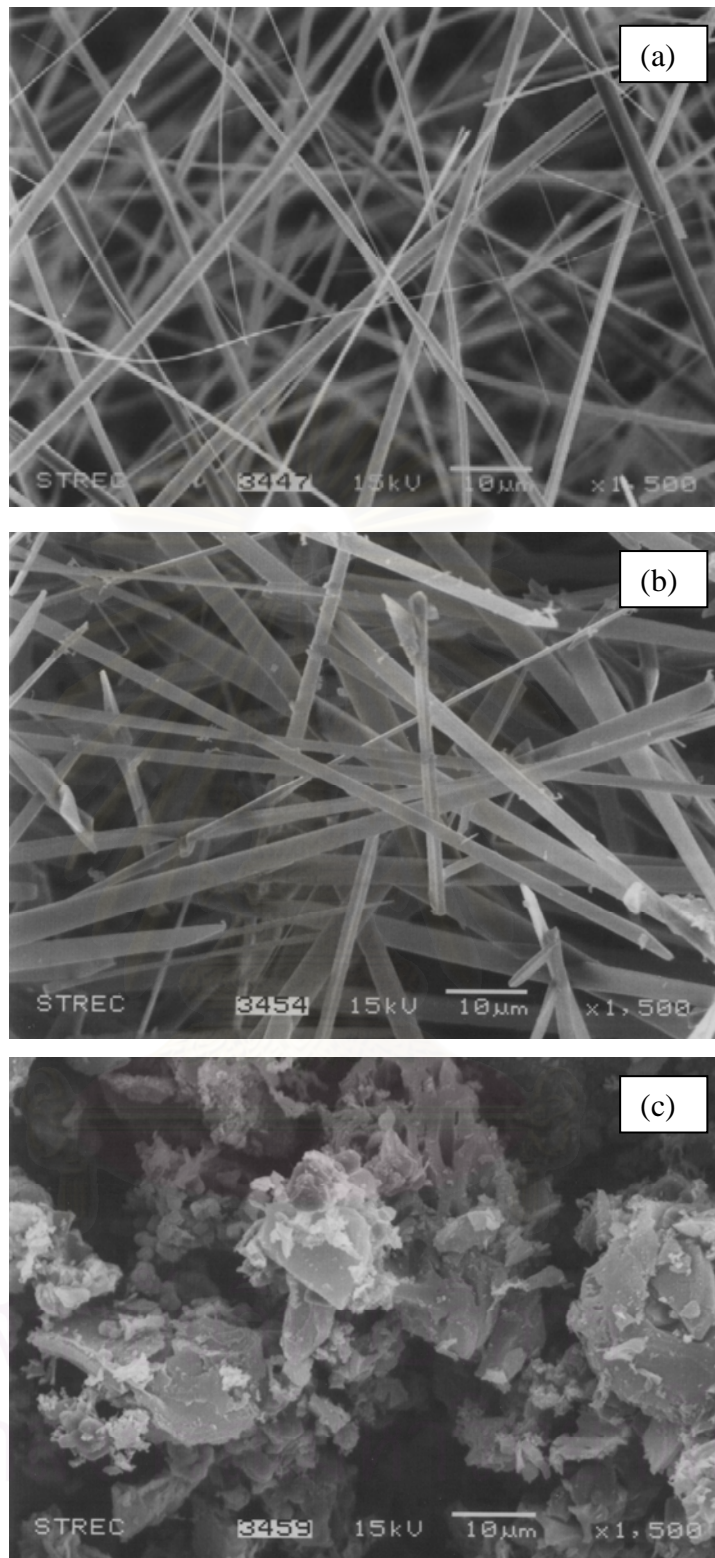
Product type	Element	Atomic Concentration (%)	Mass Concentration (%)
Dark gray powder (DGP)	O	10.18	11.35
	N	10.72	10.46
	Si	10.71	20.96
	C	68.38	57.23
White fibrous material (WFM)	O	24.63	19.92
	N	37.78	26.74
	Si	37.59	53.34
Fiber on the edge of sample tray (CWF)	O	39.72	32.03
	N	24.43	17.25
	Si	35.85	50.72

The SEM micrographs of each portion of products are shown in Figure 4.6. It is clearly indicated that morphology of product in different portions are quite different. The dark gray powder in the DGP layer consists of irregular shape aggregates mixed with rod-like grains. The electron dispersive X-ray spectroscopy (EDX) analyzer equipment on SEM revealed that the aggregates were carbon-rich, while the rod-like grains were silicon-rich, confirming the visual observation of residual carbon. For the WFM layer, they consist of long ribbon-shaped materials forming in two-dimensional. These ribbons have uniform width of approximately 3-5  $\mu\text{m}$ , thickness in sub-micron scale and length of several hundred micrometers. The tip of the ribbon is bevelled shape. Lencart-Silva and Vieira (1999) studied on the carbothermal reduction and nitridation of silica and found that the growth of silicon nitride ribbon was controlled by silicon monoxide (SiO) diffusion in a single space direction at temperature between 1300°C and 1450°C. It has been reported that

microribbons silicon nitride grow via a metal-catalyzed vapor-liquid-solid (VLS) process [Kawai and Yamakawa, 1998]. In our investigation, no catalytic metal was used. Therefore, the formation of  $\text{Si}_3\text{N}_4$  ribbon in the WFM layer should fall into the kind of a vapor-solid (VS) process. Finally, for the CWF layer, it is consisted of collection of round and smooth fibers, with diameter in the range of 1 to 3  $\mu\text{m}$ . The length of these fibers are in the millimeter range. The fact that the CWF layer is found outside the cavity of the sample holder suggests that it is grown from vapor phase. Since the fibers are composed of silicon, it further suggests that siliceous vapor was generated from the RHA starting powder, carried out of the sample holder, and reacted with nitrogen gas to form the fibers and ribbons outside the sample holder according to Eq.2.9. No sign of liquid, e.g. melting or bead forming at the tip of the fiber, was observed from SEM images (Figure 4.6a). This is indicated that the fiber grows by VS mechanism, rather than VLS mechanism.



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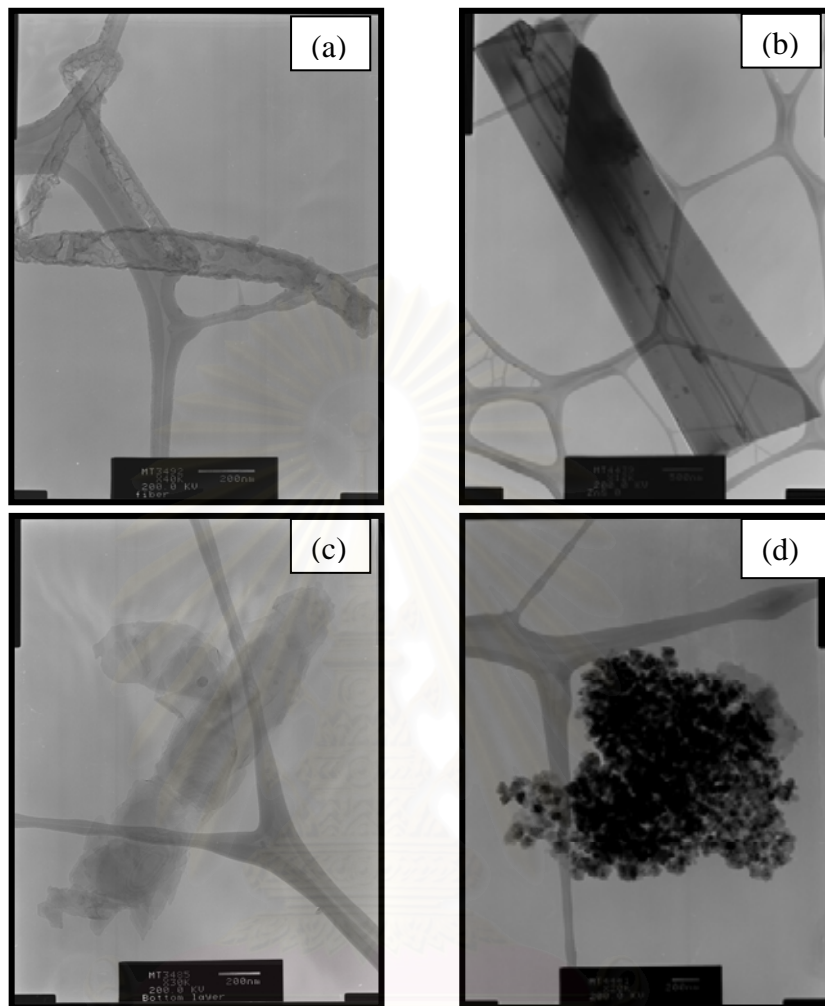
**Figure 4.6** SEM micrographs of products from the carbothermal reduction and nitridation at 1450°C for 6h: (a) cotton-like white fibers on the edge of sample holder (CWF), (b) white fibrous top layer (WFM), (c) dark gray powder (DGP).

The generation of siliceous vapor from the bed of RHA was confirmed by inserting an ¼-inch-diameter tube directly above the sample holder to collect any vapor generated. Solid particles were found in the collecting tube because the siliceous vapor has very high melting point and it condenses around the area where the temperature of the system drops. Analysis of the collected particles by XPS revealed that the particles contain significant amount of silicon. It is therefore indicated that the RHA system generates siliceous species in vapor form.

**Table 4.3** Analysis of particles collected by placing tube above the RHA bed

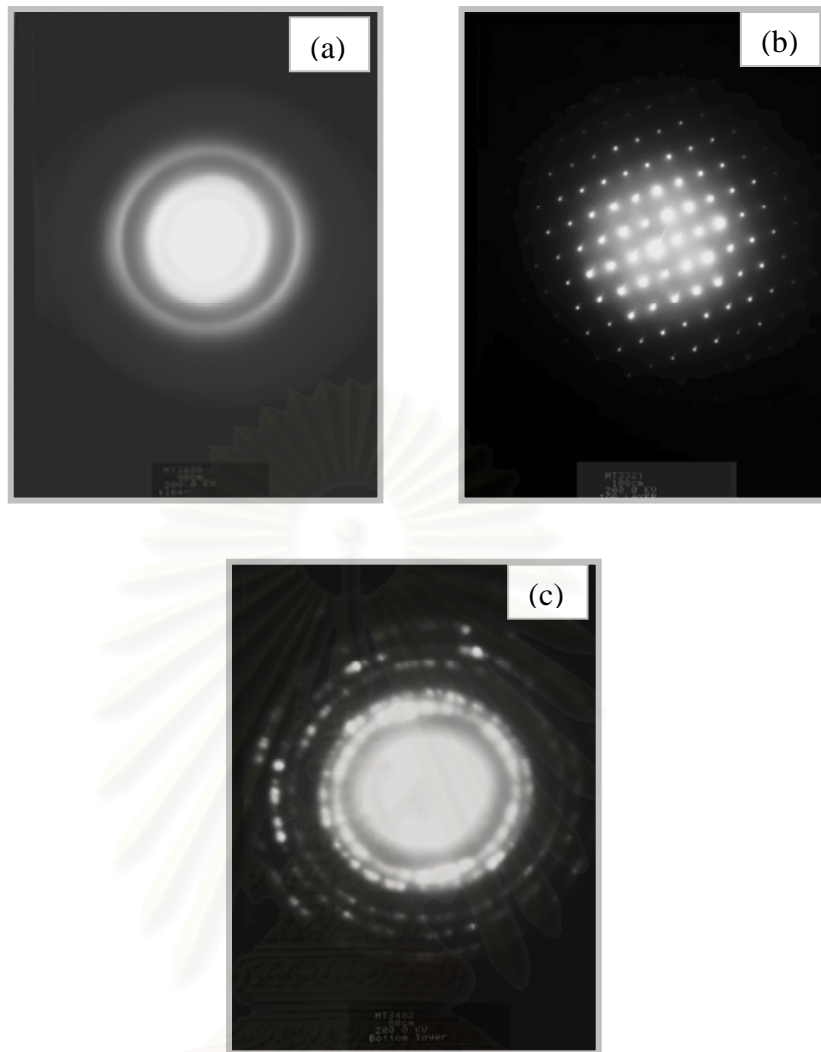
Element	Atomic Concentration (%)	Mass Concentration (%)
O	56.80	53.87
C	23.99	17.08
Si	15.70	26.13

The results from the investigation using TEM and electron diffraction, as shown in Figure 4.7 and 4.8, respectively, also support the finding from both XRD and SEM analyses. In the DGP layer, the rod-like grains are polycrystalline with high crystallinity, while the irregular shape aggregates are amorphous. The fiber on the edge of sample holder are also polycrystalline, but the crystallinity is not as high as grains in the DGP layer. On the other hand, it was found that the WFM layer is in fact a collection of silicon nitride single crystals.



**Figure 4.7** TEM micrographs of products from the carbothermal reduction and nitridation at 1450°C for 6 h:

- (a) cotton-like white fibers on the edge of sample holder (CWF)
- (b) white fibrous top layer (WFM)
- (c) rod-like grains in dark gray powder (DGP)
- (d) irregular shape aggregates in dark gray powder (DGP)



**Figure 4.8** SAED patterns of products from the carbothermal reduction and nitridation at 1450°C for 6 h:

- (a) cotton-like white fibers on the edge of sample holder (CWF)
- (b) white fibrous top layer (WFM)
- (c) rod-like grains in dark gray powder (DGP)

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When two sample holders containing same RHA were placed next to each other in series in the reactor, it was observed that mass fraction of both WFM and CWF layers in the downstream sample holders were greater than that of the upstream sample holder, shown in Table 4.4. This observation confirms the hypothesis that both WFM and CWF layers are formed from the reaction of siliceous vapor, which is generated from RHA and carried by flow of the reactant gas mixture downstream. Although the siliceous vapor has not been identified experimentally in this work, it is likely to be SiO, since involvement of SiO vapor in the carbothermal reduction and nitridation process has been generally recognized for long time [Lin and Kimura, 1996; Arik, 2003]. According to literatures, generation of silicon monoxide vapor has been suggested by the reduction of silica by carbon and carbonmonoxide as shown in Eq. 2.5 and 2.6. Thermodynamics calculation shows that SiO generation is more favored at higher temperature. Nevertheless, it has been found that the generation rate is controlled by diffusion of SiO out of the solid, from which SiO is generated [Lin, 1995].

**Table 4.4** Mass fraction of each portion of products obtained from the carbothermal reduction and nitridation process at 1450°C for 6 hours

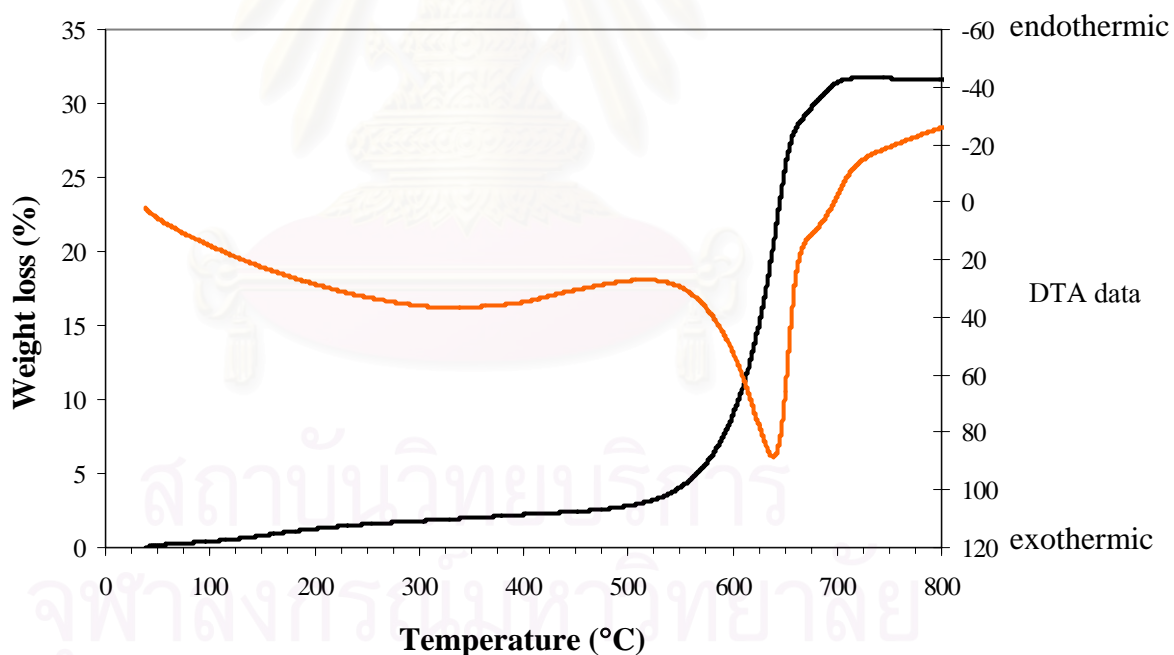
Location of sample tray	Sample mass change <sup>(a)</sup> (%)	Mass fraction of product (%)		
		Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)
upstream	-58.27	86.15	13.37	0.48
downstream	-55.02	73.71	18.15	7.78

<sup>(a)</sup> indicates mass loss after the carbothermal reduction and nitridation process.

(a)  
Minus sign



The results from all analytical techniques discussed above have suggested that silicon nitride can be successfully synthesized from RHA without major contamination from other crystalline phases. However, residue of carbonaceous compound from RHA in the product, especially in the bottom layer, is expected. The thermogravimetric analysis and differential thermal analysis (TG/DTA) were conducted to verify the presence of residual carbon and investigate whether it could be removed by oxidation. For TG/DTA experiment, the sample was heated to 900°C at heating rate of 20°C/min in alumina pan under flow of oxygen. The results, shown in Figure 4.9, reveal that carbon remains only in the DGP layer. Amount of residual carbon is approximate 30-35% in the product from the reaction at 1450°C for 6 h. Figure 4.9 indicates that mass loss is significant at about 200°C, and the trend continues up to 670°C and remains constant at 700°C. However, the remaining carbon has been proved to be removable by simple oxidation. When all carbon is removed, the sample turns light gray which is corresponding to the color of silicon nitride.



**Figure 4.9** TG/DTA of products from the carbothermal reduction and nitridation at 1450°C for 6 h.

### 4.3 Effects of Reaction Temperature

In this section, effects of reaction temperature on the carbothermal reduction and nitridation of RHA are investigated using fixed reaction time of 6 h. The reaction temperature investigated is in the range of 1400-1470°C, since the preliminary experiments have shown that silicon nitride can not be synthesized via the carbothermal reduction and nitridation at temperature below 1400°C. The results are shown in Table 4.5.

**Table 4.5** Mass fraction of each portion of products obtained from the carbothermal reduction and nitridation process at various temperatures.

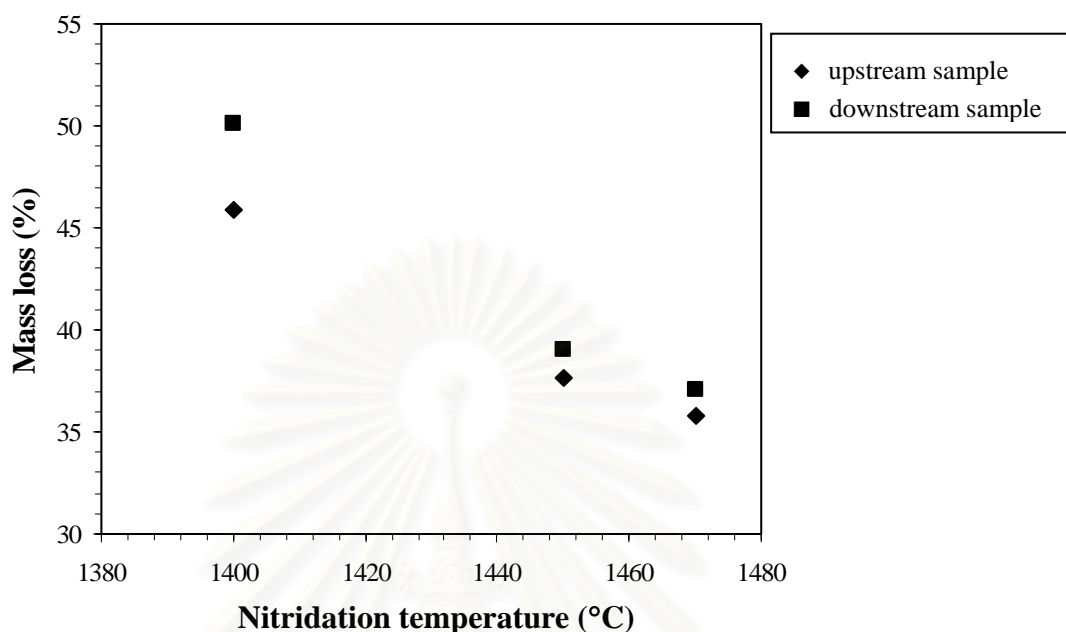
Reaction temperature (°C)	No. of sample tray <sup>(a)</sup>	Sample mass change <sup>(b)</sup> (%)	Mass fraction of product (%)		
			Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)
1400	1	-49.15	91.65	7.96	0.39
	2	-47.30	87.10	11.48	1.42
1450	1	-58.27	86.15	13.37	0.48
	2	-55.02	73.71	18.15	7.78
1470	1	-57.45	79.63	14.53	5.84
	2	-48.15	70.46	17.53	12.04

<sup>(a)</sup> 1 represents sample in the upstream sample holder, while 2 represents sample downstream.

<sup>(b)</sup> Minus sign indicates mass loss after the carbothermal reduction and nitridation process.

The results show that reaction temperature has significant effect on mass fraction of each product type, especially the CWF and DGP portion. The higher the temperature, the greater the amount of fibers in CWF portion. On the contrary, higher reaction temperature results in smaller fraction of the DGP. Since vapor pressure of silicon monoxide increases with temperature, silicon monoxide generation is more favored at higher temperature, resulting in greater amount long fibers formed as CWF layer. At the same time, more free carbon in RHA is consumed during the generation of silicon monoxide vapor at higher temperature, according to Eq. 2.5. The TG/DTA results also confirm that residual carbon in the DGP portion decreases with higher nitridation temperature. The mass loss of the product in DGP portion, observed in

TG/DTA, is significantly reduced when the nitridation takes place at 1450°C. This is responsible for a decrease in mass fraction of the DGP layer.



**Figure 4.10** Results from TG/DTA analysis for the DGP portion of product synthesized at various temperatures.

The result in Figure 4.10 also indicates that the amount of carbon residue in the DGP layer of the product downstream is greater than that of the upstream product. It is possibly due to the fact that silicon monoxide generated from the upstream sample is carried by the reactant gas downstream. Since vapor pressure of silicon monoxide is very low, generation of silicon monoxide vapor from the downstream sample holder, which is covered by silicon monoxide vapor carried from upstream, is less spontaneous. Therefore, carbon, which is normally consumed during silicon monoxide generation, remains in the DGP layer.

As mentioned earlier, silicon monoxide vapor can be produced by reduction of silica by either carbon (Eq. 2.5) or carbon monoxide (Eq. 2.6). In spite of being thermodynamically less favored than Eq. 2.5, some authors have assumed that Eq. 2.6 is primarily responsible for the formation of silicon monoxide because contact between silica and carbon particle is limited [Wei et al., 1984; Chrysanthou et al., 1991; Liou and Chang, 1995]. In turn, it has been proposed that the formation of

silicon nitride from carbothermal reduction and nitridation process is strongly dependent on the concentration of CO in the vicinity of the sample. The CO concentration is increased, when the reaction temperature increases from 1400 to 1470°C [Silva and Figueiredo, 2001]. However, in case of RHA, silicon and carbon is naturally blend in very high homogeneity. Limitation of reaction in Eq. 2.5 due to silica and carbon contact is significantly reduced. Therefore, Eq. 2.5 may also play an important role in the nitridation process of RHA.



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#### 4.4 Effect from Gas Phase

In this section, an involvement of silicon monoxide vapor is further investigated by varying the overall flow rate of the reactant gas mixture, which is nitrogen mixed with 10% hydrogen. The ranges of overall flow rate investigated are 30-70 l/h. The results are shown in Table 4.6.

**Table 4.6** Mass fraction of each portion of products obtained from the carbothermal reduction and nitridation process using different flow rates of reactant gas.

Overall flow rate (l/h)	No. of sample tray <sup>(a)</sup>	Sample mass change <sup>(b)</sup> (%)	Mass fraction of product (%)		
			Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)
30	1	-55.94	77.12	22.20	0.68
	2	-49.93	72.20	14.00	13.80
50	1	-58.27	86.15	13.37	0.48
	2	-55.02	73.71	18.15	7.78
70	1	-59.05	70.39	25.48	4.13
	2	-52.48	63.85	19.85	16.30

<sup>(a)</sup> 1 represents sample in the upstream sample holder, while 2 represents sample downstream.

<sup>(b)</sup> Minus sign indicates mass loss after the carbothermal reduction and nitridation process.

Although the reactant gas flow rate did not significantly affect the mass fraction of each type of products, an increase in the overall gas flow rate resulted in higher fraction of long fibers. As discussed in prior sections, these fibers are grown from silicon monoxide vapor by vapor-solid (VS) mechanism. Therefore, an increase in the production of silicon monoxide results in higher growth of fibers. The result is clear that the increased flow rate reduces the gas film mass transfer resistance for the diffusion of silicon monoxide vapor from RHA bed to bulk gas stream. Moreover, since the vapor pressure of silicon monoxide vapor at temperature of system is very low, silicon monoxide vapor generated must be continuously removed by the flow of gas in the reactor, in order to sustain its production [Lin and Kimura, 1996]. Copious flow of reactant gas ensures adequate nitrogen gas for conversion to silicon nitride. This also prevents the formation of  $\beta$ -SiC or  $\text{Si}_2\text{N}_2\text{O}$  by reducing the partial pressure

of the other gaseous species [Durham et al., 1991]. Ekelund and Forslund (1992) have reported that small amounts of CO (~1%) produced from the system would obstruct the formation of silicon nitride. Hence, a higher flow rate of reactant gas would be favorable in maintaining low CO concentration and also provides more efficient reaction of SiO with N<sub>2</sub> to form Si<sub>3</sub>N<sub>4</sub>.

Effects of gas phase were further investigated by studying the effect of gas composition, especially hydrogen, in the reactant gas mixture. Since the reactant gas mixture is consisted of nitrogen and hydrogen, change in concentration of hydrogen also affects the concentration of nitrogen in the system. Therefore, it would be inconclusive whether any effect observed is the result from changing in concentration of hydrogen or nitrogen. In this section, nitrogen concentration is fixed, while varying the concentration of hydrogen in the range of 0-40%. Argon is used as an inert balance to keep the overall flow rate constant at 80 l/h. The reaction was conducted at 1450°C for 6 h. The results are shown in Table 4.7.

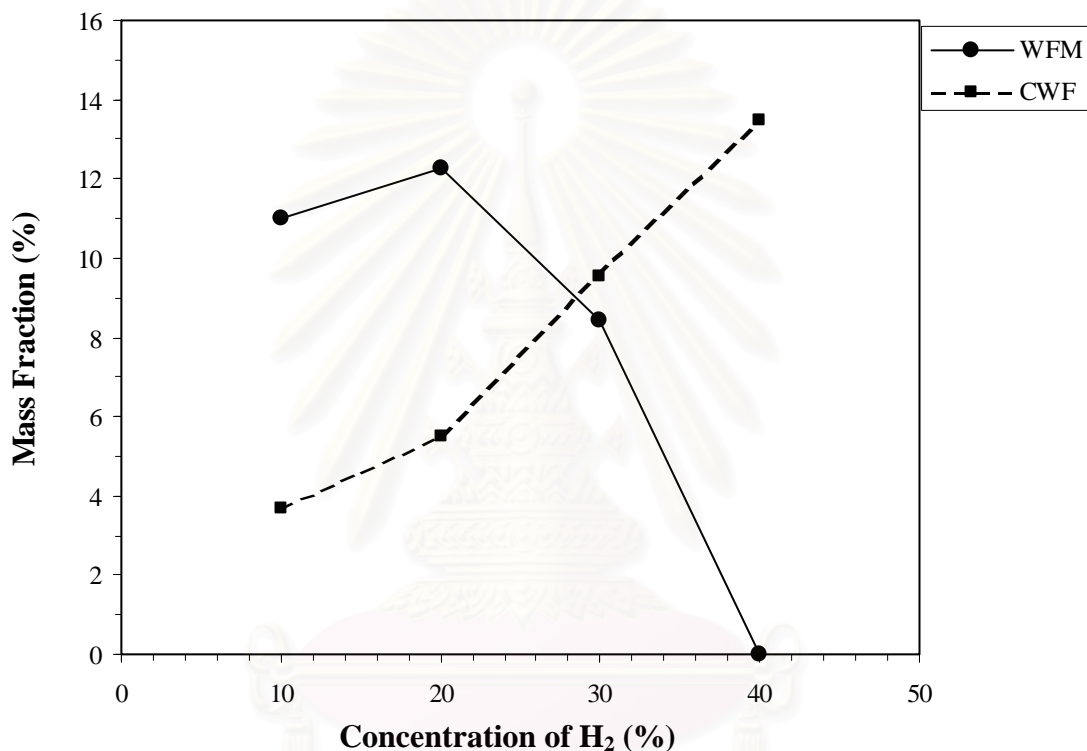
**Table 4.7** Mass fraction of each portion of products obtained from the carbothermal reduction and nitridation process at 1450°C for 6 hours using various values of hydrogen concentration.

Concentration of H <sub>2</sub> (%)	No. of sample tray <sup>(a)</sup>	Sample mass change <sup>(b)</sup> (%)	Mass fraction of product (%)		
			Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)
0	1	-33.28		No reaction	
	2	-28.45		No reaction	
10	1	-57.42	90.64	9.36	-
	2	-54.73	85.30	11.00	3.70
20	1	-60.07	91.78	8.22	-
	2	-56.77	82.23	12.27	5.5
30	1	-65.78	90.78	9.22	-
	2	-60.64	82.05	8.41	9.54
40	1	-67.45	100	-	-
	2	-62.67	86.53	-	13.47

<sup>(a)</sup> 1 represents sample in the upstream sample holder, while 2 represents sample downstream.

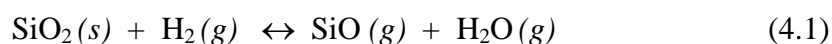
<sup>(b)</sup> Minus sign indicates mass loss after the carbothermal reduction and nitridation process.

It has been reported in literature that gas-phase composition has a great influence on the formation of silicon nitride fibers [Sucik et al., 2003]. In this work, the results confirm that composition of gas mixture have significant effect on the mass fraction of each type of product, especially the WFM and CWF portion. More importantly, it is found that the presence of hydrogen in the system is necessary for the carbothermal reduction and nitridation process. The product from the nitridation under pure N<sub>2</sub> atmosphere is silica in cristobalite phase with no silicon nitride.



**Figure 4.11** Relation between mass fraction of product from downstream sample holder with concentration of H<sub>2</sub>

Amount of fibers in CWF portion increases when the concentration of hydrogen is increased, as shown in Figure 4.11. These results confirm that hydrogen in the reactant gas mixture influences the generation of silicon monoxide from RHA and also the formation of fibers. Silva and Figueiredo (2001) have reported that the presence of hydrogen in the atmosphere causes the direct reduction of silica according to Eq. 4.1 and increase the yield of the reaction between silica and carbon.



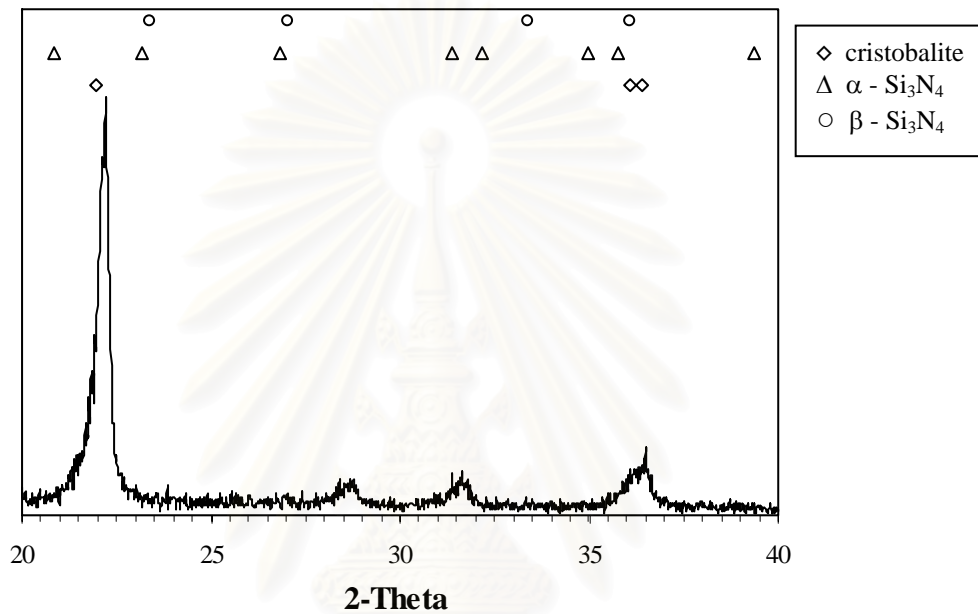
It should be noted that no long fibers (CWF layer) is observed on the upstream sample holder. This should be the result from very high flow rate of the reactant gas employed (80 l/h). Majority of silicon monoxide vapor generated from RHA in the upstream sample holder is carried away downstream, where long fibers are formed.

For the WFM portion, small amount of hydrogen enhances its formation. However an increase in hydrogen concentration beyond 20% results in a decrease in the amount of fibrous material in the WFM layer. At the hydrogen concentration of 40%, only light gray powder in the DGP portion and long fiber in the CWF portion are formed without the WFM layer. It should also be emphasized that the color of the product in DGP portion is lighter when high concentration of hydrogen is used. These results indicate that reaction between solid silica and nitrogen gas at the hydrogen concentration of 40% is more spontaneous. It is also proved by decreasing amount of RHA used by 50% to get the thickness of RHA bed reduced by approximately 50%, and using hydrogen concentration of 20%. The product obtained is similar to that described earlier. Only two portions, i.e. light gray powder in DGP portion and fiber in CWF portion are found. These results indicate that hydrogen in the system not only affects the generation of silicon monoxide and formation of fibers, but also has beneficial effect in accelerating the rate of nitridation in solid phase of DGP portion. Both thickness of RHA bed in the sample holder and concentration of hydrogen in reactant gas mixture have significant effect on fraction of each portion in product.

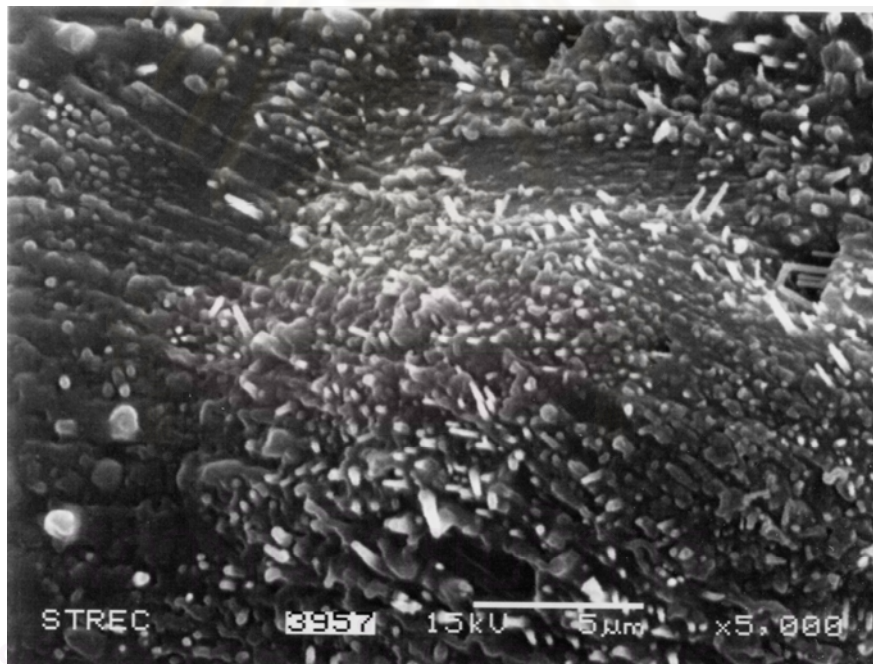
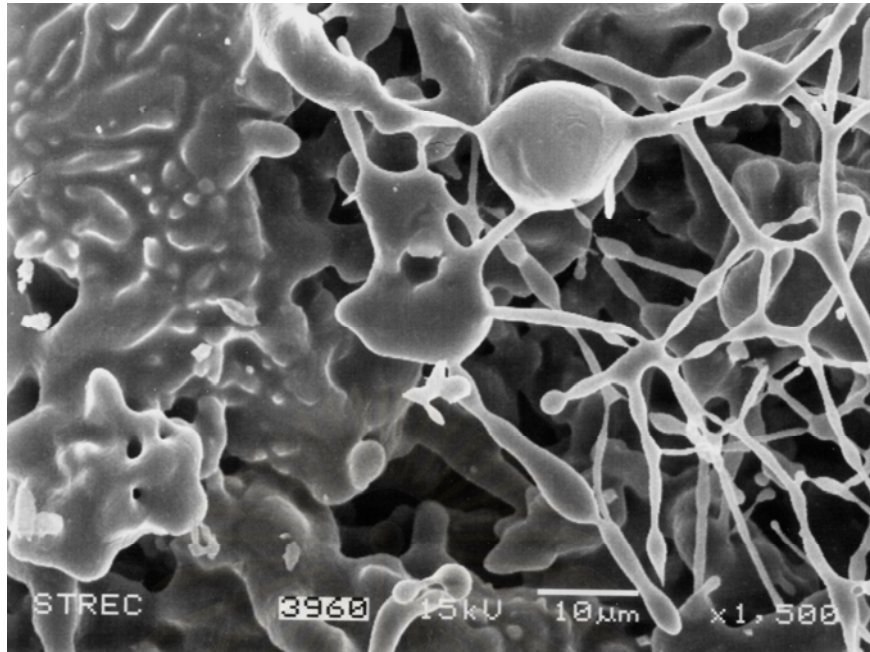
In comparison, steam was used instead of hydrogen gas for the carbothermal reduction and nitridation process at 1450°C for 6 h, by passing the nitrogen gas through water before entering the reactor. The vapor pressure of steam at room temperature is 4.183 kPa and, therefore, the concentration of steam in the reactant gas is 4.13%. It was found that mass loss of products in the upstream sample holder and the downstream sample holder were 60.6% and 61.5%, respectively. X-ray diffraction analysis shown in Figure 4.12 indicated that the resulting product is cristobalite. No silicon nitride was obtained. It has been generally recognized that cristobalite is the most chemically stable form of silica. The SEM micrographs of products are shown in



Figure 4.13. It is clearly seen that morphology of product is different than the product synthesized when hydrogen is used in reactant gas mixture. The results that the mechanism of the carbothermal reduction and nitridation of RHA using nitrogen mixed with hydrogen is different than that using nitrogen mixed with steam. However, exact role of hydrogen is still unclear and detailed study to verify the actual mechanism is needed.



**Figure 4.12** XRD pattern of product from the carbothermal reduction and nitridation at 1450°C for 6 h using steam instead of hydrogen gas.



**Figure 4.13** SEM micrographs showing various morphologies of products obtained from the carbothermal reduction and nitridation at 1450°C for 6 h when steam is used instead of hydrogen gas.

#### 4.5 Effects of Reaction Time

The reaction time of 3, 6 and 10 hours were investigated in this work. When the reaction duration was prolonged, amount of the dark gray powder in DGP layer decreased, while both white cotton-like fibers in DWF layer and fibrous in WFM layer of the product in the sample holder increased. The results are shown in Table 4.8. Visual observation showed that the fibers were longer in length when the reaction time was lengthened indicating that the fibers continue growing over time. Majority of the product obtained after 10 hours of the reaction was fibers, especially on the downstream sample holder. On the contrary, when the reaction period was limited to only 3 hours, majority of the product obtained was dark gray powder with very thin layer of white fibrous layer formed on top. No fibers on the edge of the sample holder was observed. These results indicate that the carbothermal reduction and nitridation process of RHA is rather slow. The process does not reach the stage of slow progress (or complete conversion of the reactants) even after 6 hours of the operation. This is in agreement with the results reported earlier in the literature for the carbothermal reduction and nitridation of silica [Lencart-silva and Vieira, 1999].

**Table 4.8** Mass fraction of each portion of products obtained from the carbothermal reduction and nitridation process for various reaction periods.

Reaction time (h)	No. of sample tray <sup>(a)</sup>	Sample mass change <sup>(b)</sup> (%)	Mass fraction of product (%)		
			Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)
3	1	-52.50	100	-	-
	2	-56.50	100	-	-
6	1	-58.27	86.15	13.37	0.48
	2	-55.02	73.71	18.15	7.78
10	1	-60.45	66.33	28.88	4.79
	2	-43.73	46.37	30.35	23.27

<sup>(a)</sup> 1 represents sample in the upstream sample holder, while 2 represents sample downstream.

<sup>(b)</sup> Minus sign indicates mass loss after the carbothermal reduction and nitridation process.

#### 4.6 Effects of Rice Husk Pretreatment

Two types of rice husk pretreatment are employed in this work, i.e. washing in distilled water and acid treatment using hydrochloric acid. The pretreatment is done before pyrolysis of rice husk to RHA. The results from quantitative analysis carried out by the X-ray Photoelectron Spectroscopy (XPS), as shown in Table 4.9, reveal that SiO<sub>2</sub> content in RHA sample pretreated in hydrochloric acid is slightly higher than the sample treated in distilled water, which is in agreement with the findings in literature [Sugita et al., 2004]. Moreover, according to literature survey as shown earlier in Table 2.2, the amount of impurities decreases substantially after acid leaching. This report indicates that acid treatment of rice husk (ATRH) have a significant effect on the chemical composition of the rice husk ash after pyrolysis. Similar data were also reported by Amick (1982), Chakraverty (1988) and Andreoli (2000). For the study of pretreatment effect, the reaction is conducted at temperature in the range of 1400-1470°C for 3 to 10 h with the overall flow rate of the gas mixture, nitrogen mixed with 10% hydrogen, at 50 l/h.

**Table 4.9** Elemental composition of RHA with different pretreatments, obtained by the X-ray Photoelectron spectroscopy (XPS).

Element	RHA pretreated with distilled water		RHA pretreated with hydrochloric acid	
	Atomic Concentration (%)	Mass Concentration (%)	Atomic Concentration (%)	Mass Concentration (%)
O	26.99	29.93	25.31	27.97
C	64.65	53.80	65.63	54.45
Si	8.36	16.27	9.06	17.58

The results of the carbothermal reduction and nitridation of the acid treated rice husk ash (ATRH) at various reaction temperatures and reaction times shown in Table 4.10 and Table 4.11, respectively. The XRD patterns of products in each

portion, as shown in Figure 4.14, confirm that silicon nitride is the major crystalline phase in all product types. No other apparent crystalline phase is detected.



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**Table 4.10** Mass fraction of each portion of products obtained from the carbothermal reduction and nitridation process of ATRH and RHA for 6 hours at various temperatures.

Reaction temperature (°C)	No. of sample tray <sup>(a)</sup>	ATRH				RHA			
		Sample mass change <sup>(b)</sup> (%)	Mass fraction of product (%)			Sample mass change <sup>(b)</sup> (%)	Mass fraction of product (%)		
			Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)		Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)
1400	1	-51.17	98.26	1.74	-	-49.15	91.65	7.96	0.39
	2	-51.81	80.99	18.39	0.62	-47.30	87.10	11.48	1.42
1450	1	-57.14	96.62	3.38	-	-58.27	86.15	13.37	0.48
	2	-56.51	83.59	13.20	3.21	-55.02	73.71	18.15	7.78
1470	1	-60.77	91.72	8.15	0.13	-57.45	79.63	14.53	5.84
	2	-59.43	76.26	18.08	5.67	-48.15	70.46	17.53	12.04

<sup>(a)</sup> 1 represents sample in the upstream sample holder, while 2 represents sample downstream.

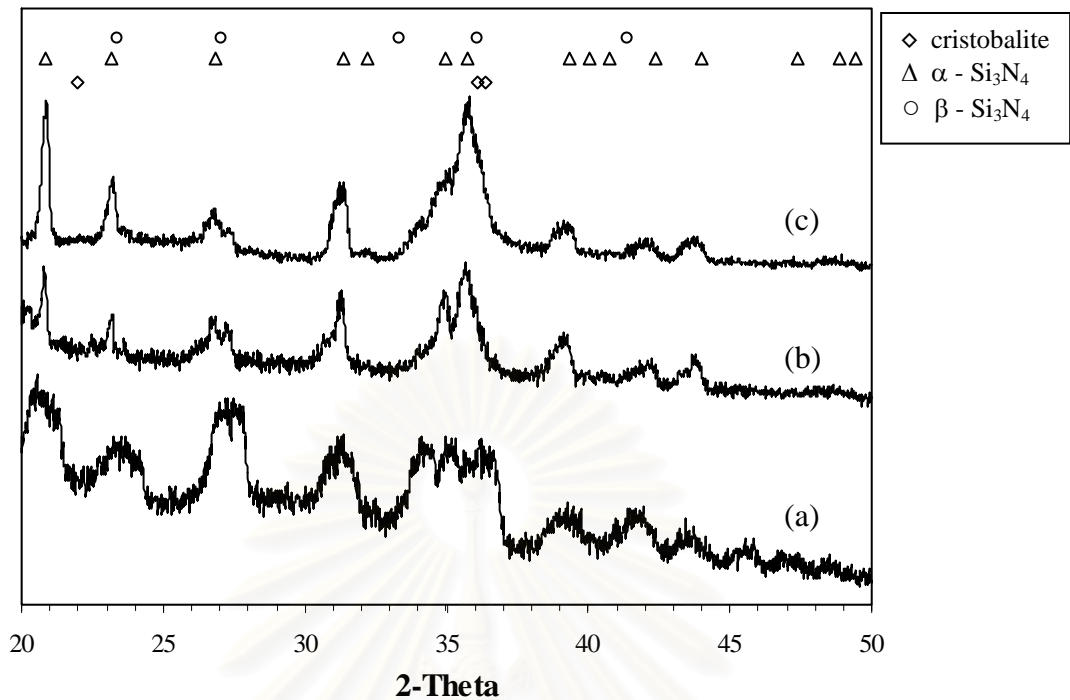
<sup>(b)</sup> Minus sign indicates mass loss after the carbothermal reduction and nitridation process.

**Table 4.11** Mass fraction of each portion of products obtained from the carbothermal reduction and nitridation process of ATRH and RHA at 1450 °C for various reaction times.

Reaction time (h)	No. of sample tray <sup>(a)</sup>	ATRH				RHA			
		Sample mass change <sup>(b)</sup> (%)	Mass fraction of product (%)			Sample mass change <sup>(b)</sup> (%)	Mass fraction of product (%)		
			Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)		Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)
3	1	-50.4	87.94	12.06	-	-52.50	100	-	-
	2	-49.5	82.93	14.60	2.47	-56.50	100	-	-
6	1	-57.14	96.62	3.38	-	-58.27	86.15	13.37	0.48
	2	-56.51	83.59	13.20	3.21	-55.02	73.71	18.15	7.78
10	1	-62.24	83.53	16.47	-	-60.45	66.33	28.88	4.79
	2	-54.99	61.35	26.58	12.07	-43.73	46.37	30.35	23.27

<sup>(a)</sup> 1 represents sample in the upstream sample holder, while 2 represents sample downstream.

<sup>(b)</sup> Minus sign indicates mass loss after the carbothermal reduction and nitridation process.

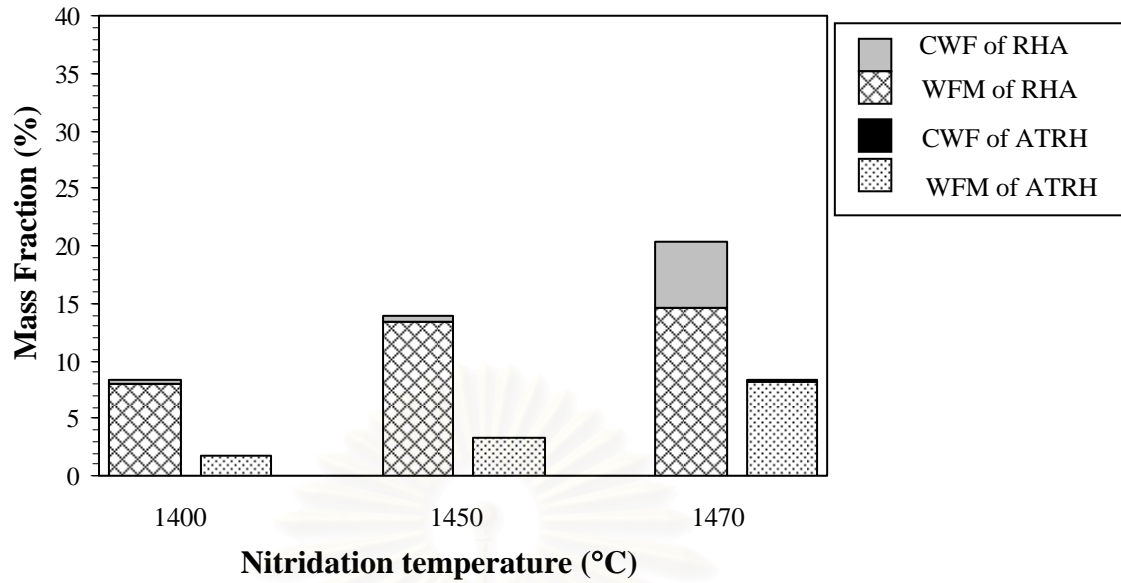


**Figure 4.14** XRD patterns of products from the carbothermal reduction and nitridation of ATRH at 1450°C for 6 h:

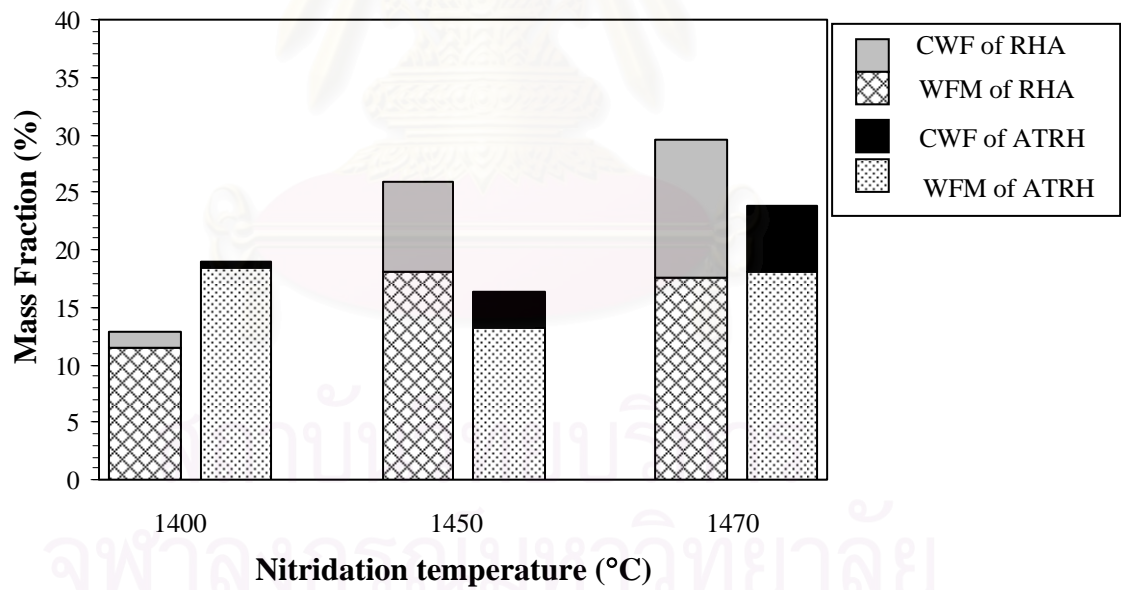
- (a) cotton-like white fibers on the edge of sample holder (CWF).
- (b) white fibrous top layer (WFM).
- (c) dark gray powder (DGP).

For better comparison, effect of reaction temperature between products from carbothermal reduction and nitridation process of RHA with ATRH was investigated, as shown in Figures 4.15 and 4.16. The results show that mass fraction of both CWF and WFM portions of the product synthesize from ATRH is less than when RHA is used. However, it should be noted that the DGP portion of product using ATRH as starting material is lighter in color, comparing to the DGP portion of product from normal RHA. It suggests that the formation of silicon nitride via gas-solid reaction, according to Eq. 2.4 is enhanced in case of ATRH. This may be the result from the enhanced surface area of ATRH, implying from much better nitrogen adsorption of ATRH, as shown in Table 2.2.

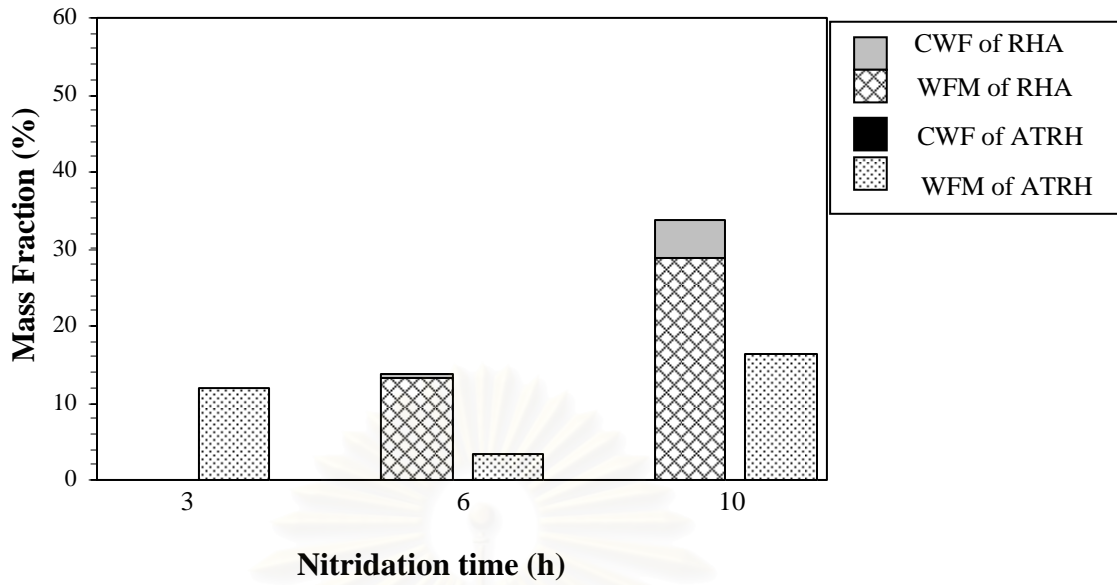




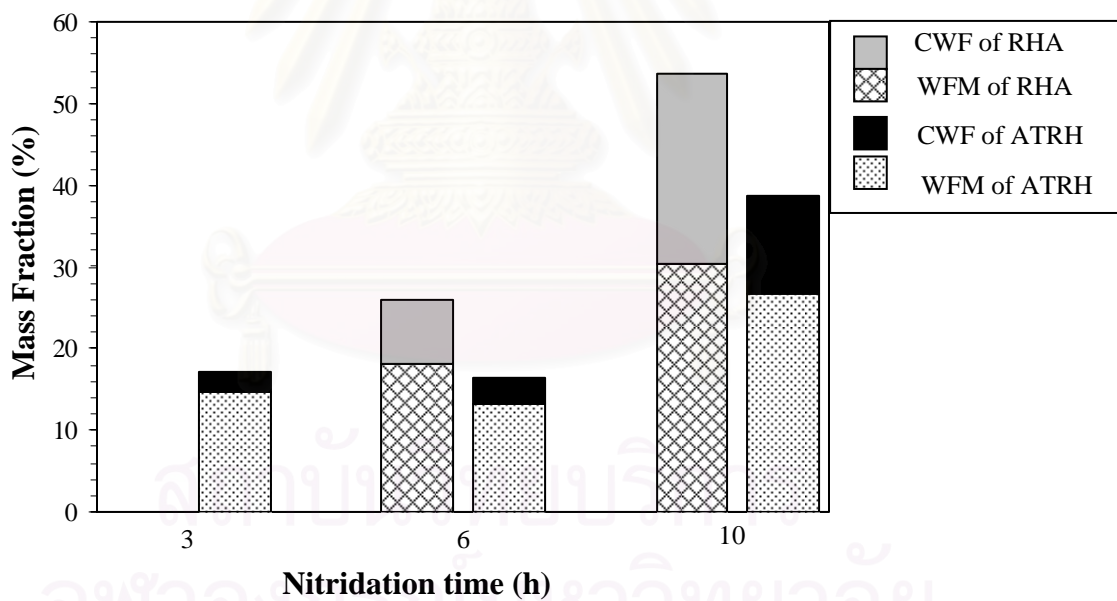
**Figure 4.15** Comparison of mass fraction of CWF and WFM layers of products in *upstream* sample holder obtained from the nitridation of RHA and ATRH at *various temperatures*.



**Figure 4.16** Comparison of mass fraction of CWF and WFM layers of products in *downstream* sample holder obtained from the nitridation of RHA and ATRH at *various temperatures*.



**Figure 4.17** Comparison of mass fraction of CWF and WFM layers of products in *upstream* sample holder obtained from the nitridation of RHA and ATRH at *various times*.



**Figure 4.18** Comparison of mass fraction of CWF and WFM layers of products in *downstream* sample holder obtained from the nitridation of RHA and ATRH at *various times*.

#### 4.7 Comparative Study using Silica Mixed with Excess Carbon

For comparison, amorphous silica mixed with 50% excess carbon was subjected to the carbothermal reduction and nitridation process at 1450°C for 3 and 6 h, respectively. It was found that products obtained consisted of two types of products, i.e. dark gray powder in DGP portion and thin layer of white fibrous material in WFM portion. No fiber was observed outside the cavity of the sample holder. The mass fraction data for both runs are shown in Table 4.12.

**Table 4.12** Mass fraction of each portion of products obtained from the carbothermal reduction and nitridation process of silica mixed with excess carbon.

Reaction time (h)	No. of sample tray <sup>(a)</sup>	Sample mass change <sup>(b)</sup> (%)	Mass fraction of product (%)		
			Bottom portion (DGP)	Top portion (WFM)	Long fiber on the edge of sample tray (CWF)
3	1	-53.75	69.67	30.33	-
	2	-53.92	70.95	29.05	-
6	1	-61.82	62.93	37.07	-
	2	-63.37	64.35	35.65	-

<sup>(a)</sup> 1 represents sample in the upstream sample holder, while 2 represents sample downstream.

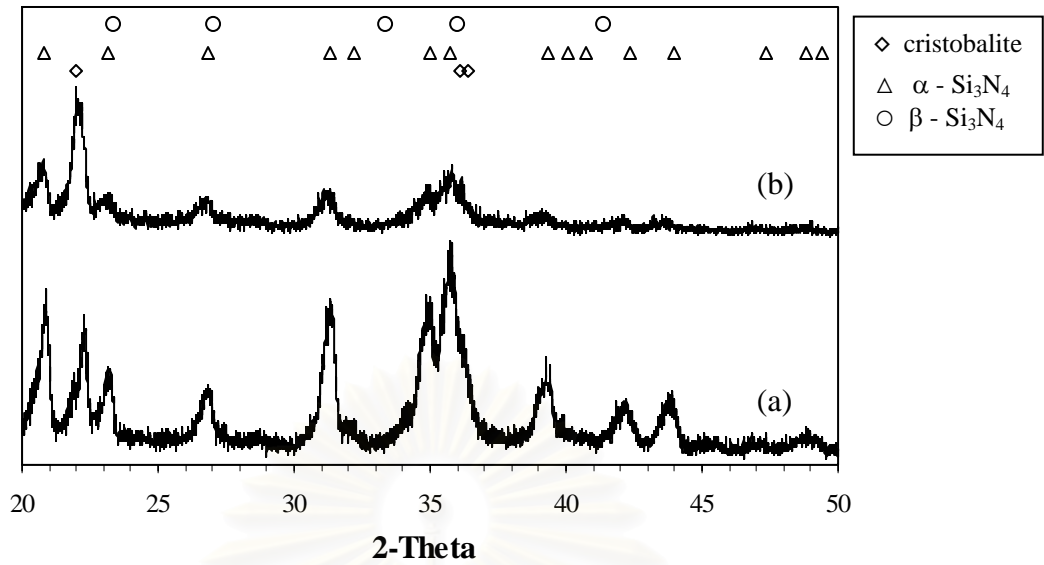
<sup>(b)</sup> Minus sign indicates mass loss after the carbothermal reduction and nitridation process.

It should be noted that no cotton-like fiber is observed on the edge of the sample holder when silica is used. Furthermore, the fraction of DGP and WFM layers in this case does not depend upon the location of the sample. This is different from the reaction when RHA is used as starting material. The results imply that no significant amount of silicon monoxide is generated when silica is used instead of RHA.

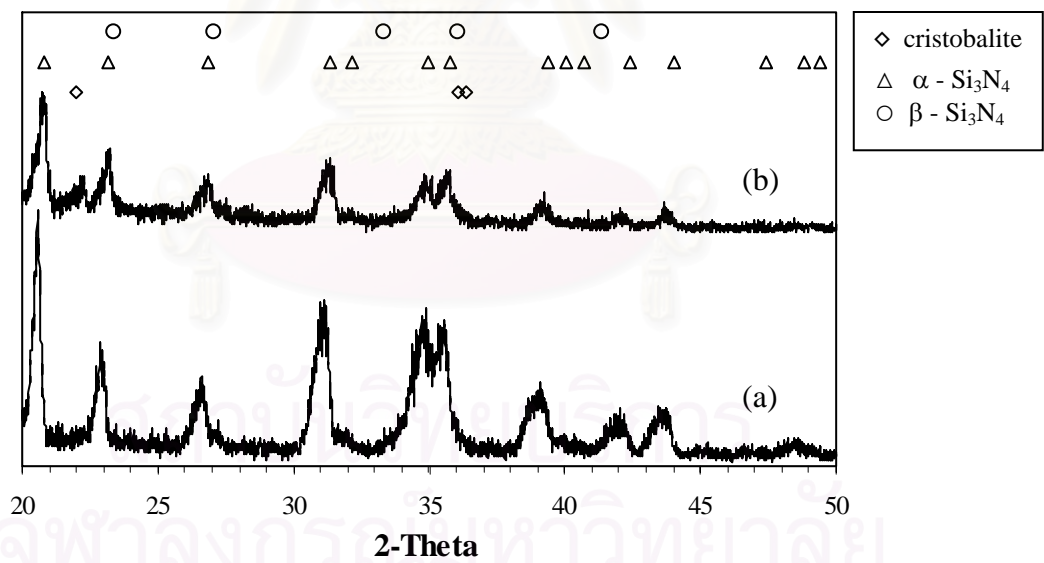
The XRD analysis in Figures 4.19 and 4.20 reveals that both portions of all samples synthesized by using silica as starting material synthesized are silicon nitride mixed with cristobalite excepted the fibrous material in WFM portion synthesized at 1450°C for 6 h. The result indicates that if amorphous silica mixed with 50% excess carbon is used as starting material, reaction time for formation silicon nitride without cristobalite are longer. Since cristobalite is one of the most stable forms of crystalline silica, silicon nitride production via carbothermal reduction of silica is indirectly retarded. Longer reaction period is required to accomplish the reduction of cristobalite by carbon.

The results from the preliminary study have suggested that the formation of cristobalite in this system takes place at temperature as low as 1000°C, which is significantly lower than the temperature for the carbothermal reduction process. Although the rate of cristobalite formation may not be as fast as the rate of silicon nitride formation due to the fact that silicon nitride can still be synthesized, cristobalite is unavoidable impurity. Removal of cristobalite from silicon nitride product is difficult. Therefore, the use of RHA as starting material is more advantageous because no cristobalite is formed.

The results also suggest that the mechanism of the carbothermal reduction and nitridation of RHA is different than that of pure silica. Detailed study to verify the actual mechanism is needed.



**Figure 4.19** XRD patterns of products from the carbothermal reduction and nitridation of silica mixed with excess carbon at 1450°C for 3 h:  
 (a) white fibrous top layer (WFM).  
 (b) dark gray powder (DGP).



**Figure 4.20** XRD patterns of products from the carbothermal reduction and nitridation of silica mixed with excess carbon at 1450°C for 6 h:  
 (a) white fibrous top layer (WFM).  
 (b) dark gray powder (DGP).

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATION

#### 5.1 Conclusions

In this work, the effects of reaction parameters on carbothermal reduction and nitridation of rice husk ash for silicon nitride synthesis were investigated. The results are summarized in the following sections.

##### 5.1.1 Preliminary experiments

- The RHA burning under uncontrolled temperature and atmosphere can not be used for the synthesis of silicon nitride, because silica in cristobalite phase is generated.
- Silicon nitride synthesis via the carbothermal reduction and nitridation of RHA is unflavored at temperature lower than 1400°C.
- Hydrogen in reaction gas is necessary for the nitridation.

##### 5.1.2 The carbothermal reduction and nitridation of RHA

• The products obtained from carbothermal reduction and nitridation of RHA can be classified into three portions, i.e. dark gray powder of silicon nitride grains mixed with residual amorphous carbon at the bottom of the sample holder (DGP), a layer of white fibrous material which is in fact ribbon shaped silicon nitride single crystals on top of the dark gray layer (WFM) and cotton-like white fibers, which are also polycrystals on the edge of sample holder (CWF). In all product types, silicon nitride is the major crystalline phase. Although carbonaceous compound remains in the product, it can be removed by an oxidation process.

• Silicon nitride in both DGP and WFM layer are  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> with no trace of  $\beta$ -Si<sub>3</sub>N<sub>4</sub>. On the contrary, the CWF portion includes the present of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> in addition to  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>.

- The formation of  $\text{Si}_3\text{N}_4$  ribbon in the WFM layer and fiber in the CWF layer is consistent with a vapor-solid (VS) mechanism.

- The generation of silicon monoxide vapor is confirmed by collecting vapor directly above the bed of RHA. It is found that, after the vapor is condensed to solid, the particles contain silicon and oxygen indicating that the system generates siliceous species.

### 5.1.3 Effect of reaction temperature

- Since vapor pressure of silicon monoxide increases with temperature, silicon monoxide generation is more favored at higher temperature, resulting in greater amount of long fibers formed as CWF layer.

- Residual carbon in the DGP portion decreases with higher nitridation temperature.

### 5.1.4 Effect from gas phase

- The increased flow rate reduces the gas film mass transfer resistance for the diffusion of silicon monoxide vapor from RHA bed to bulk gas stream, which results in higher fraction of long fibers.

- Hydrogen in the system affects the generation of silicon monoxide and formation of fibers. It is also beneficial in accelerating the rate of nitride formation in DGP portion.

- The mechanism of the carbothermal reduction and nitridation of RHA using nitrogen mixed with hydrogen is different from when nitrogen mixed with steam is used.

### 5.1.5 Effect of reaction time

- When the reaction time is prolonged, the conversion toward silicon nitride is increased but the rate of the carbothermal reduction and nitridation process of RHA is rather slow.

#### 5.1.6 Effects of the pretreated rice husk

- Gas-solid reaction between nitrogen, carbon and silica is enhanced in the carbothermal reduction and nitridation of acid-treated rice husk ash.

#### 5.1.7 Comparative studies using silica mixed with excess carbon

- Cristobalite is formed when silica is employed in the carbothermal reduction and nitridation process. It indirectly retards the formation of silicon nitride.
- The products from the carbothermal reduction and nitridation of silica mixed with carbon are different from when RHA is used as starting material. The results indicate that no significant amount of silicon monoxide is generated when silica is used instead of RHA. Therefore, the mechanism of the carbothermal reduction and nitridation of RHA is different than that of pure silica mixed with excess carbon.



## 5.2 Recommendations for Future Work

Rice husk ash is an alternative way to produce silicon nitride which is a way to minimize agricultural waste and reduce the capital investment. Therefore, it is important to discover a certain appropriate condition to produce silicon nitride from rice husk via a carbothermal reduction and nitridation. There are many critical factors involving in these processes that have not been fully investigated. Some recommendations for future work are listed as follows:

- (1) The effects of pretreated rice husk are not clear. The actual effects on nitridation rate and formation of siliceous vapor should be investigated. Moreover, type of acid for pretreatment of rice husk should also be studied.
- (2) The effects of particle size and surface area of RHA should be investigated in detail.
- (3) Silicon nitride powder synthesized should be fabricated into silicon nitride article and tested for physical properties.
- (4) Catalytic effects of metals on the carbothermal reduction and nitridation of rice husk ash for silicon nitride synthesis should be investigated.
- (5) Large scale synthesis silicon nitride from rice husk using fluidized bed should be also studied.

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**APPENDICES**

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## APPENDIX A

### THERMODYNAMICS DATA

The following thermodynamics data are used. It should be noted that the unit of the free energy,  $\Delta G^\circ$ , is converted to kJ/mol and temperature,  $T$ , is in K.

- The free energy of formation of silicon dioxide:

$$\text{Du } et al. [1989]: \quad \Delta G^\circ = -897.05 + 0.1699T$$

$$\text{Hendry [1977]:} \quad \Delta G^\circ = -940.0 + 0.20T$$

$$\text{Colquhoun } et al. [1973]: \quad \Delta G^\circ = -902.07 + 0.1736T$$

- The free energy of formation of  $\alpha$ -silicon nitride:

$$\text{Du } et al. [1989]: \quad \Delta G^\circ = -740.15 + 0.3276T$$

$$\text{Hendry [1977]:} \quad \Delta G^\circ = -1167.3 + 0.594T$$

$$\text{Colquhoun } et al. [1973]: \quad \Delta G^\circ = -820.06 + 0.3598T$$

- The free energy of formation of silicon monoxide:

Pankratz. [1982]:

$$\Delta G^\circ = -97.006 + 6.222 \times 10^{-3} T \ln T + 1.088 \times 10^{-6} T^2 - \frac{92.466}{T} - 0.133T$$

- The free energy of formation of water vapor, according to JANAF table:

$$\text{at } 1200^\circ\text{C}: \quad \Delta G^\circ = -165.910 \text{ kJ/mol}$$

$$\text{at } 1250^\circ\text{C}: \quad \Delta G^\circ = -163.048 \text{ kJ/mol}$$

$$\text{at } 1300^\circ\text{C}: \quad \Delta G^\circ = -160.179 \text{ kJ/mol}$$

- The free energy of formation of:

$$\Delta G^\circ = A + BT + CT^2$$

for carbon monoxide;       $A = -109.885$   
    $B = -9.2218 \times 10^{-2}$   
    $C = 1.4547 \times 10^{-6}$

For carbon dioxide;       $A = -393.360$   
    $B = -3.8212 \times 10^{-3}$   
    $C = 5.0587 \times 10^{-5}$



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## APPENDIX B

### LIST OF PUBLICATIONS

1. Ruttairat Precharyutasin, Varong Pavarajarn and Piyasan Prasertdam, “Silicon Nitride Synthesis via the Carbothermal Reduction and Nitridation of Rice Husk Ash”, Third Thailand Materials Science and Technology Conference, Bangkok, Thailand, August 10-11, 2004, 181-183.
2. Ruttairat Precharyutasin, Varong Pavarajarn and Piyasan Prasertdam, “Effects of the Reaction Parameters on the Carbothermal Reduction and Nitridation of Rice Husk Ash for Silicon Nitride Synthesis”, Regional Symposium on Chemical Engineering 2004, Bangkok, Thailand, December 1-3, 2004, LS212.



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## VITA

Miss Ruttairat Precharyutasin was born on 13<sup>th</sup> August, 1980, in Saraburi, Thailand. She received her Bachelor degree of Engineering with a major in Chemical Engineering from Suranaree University of Technology (SUT) Nakhon Ratchasima, Thailand in August 2003. She continued her Master study in the same major at Chulalongkorn University, Bangkok, Thailand in June 2003.



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