รายงานวิจัยฉบับสมบูรณ์

โครงการ การสังเคราะห์ซิลิกอนไนไตรด์จากเถ้าแกลบ

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สนับสนุนโดยสำนักงานคณะกรรมการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกอ. และสกว. ไม่จำเป็นต้องเห็นด้วยเสมอไป)

บทคัดย่อ

ซิลิคอนไนไตรด์ซึ่งเป็นวัสดุโครงสร้างสำหรับการใช้งานที่มีความเครียดทางกลสูงภายใต้อุณหภูมิสูงนั้นได้ถูกสังเคราะห์โดยใช้แกลบซึ่งเป็นของเสียทางการเกษตรที่มีอยู่ในปริมาณมากเป็นสารตั้งต้น ในเบื้องต้นแล้วแกลบถูกเผาภายใต้บรรยากาศเฉื่อยที่อุณหภูมิ 600 องศาเซลเซียสเป็นเวลา 3 ชั่วโมง เพื่อให้ได้เถ้าแกลบที่มีองค์ประกอบหลักเป็นซิลิกาและคาร์บอน จากนั้นจึงนำเถ้าแกลบไปผ่านกระบวนการคาร์โบเทอร์มอลรีดักชั่นและไนไตรเดชั่นที่อุณหภูมิในช่วง 1400 ถึง 1470 องศาเซลเซียส ผลิตภัณฑ์ที่ได้นั้นสามารถจำแนกออกได้เป็น 3 ส่วน ได้แก่ ผงสีเทาเข้มที่มีคาร์บอนปะปนอยู่ที่ก้นของภาชนะใส่สารตัวอย่าง ชั้นของวัสดุที่มีลักษณะเป็นเส้นใยสั้นสีขาวที่ด้านบนของสารสีเทาเข้ม และเส้นใยยาวที่ขอบของภาชนะใส่สารตัวอย่าง ผลจากการวิเคราะห์ยืนยันว่าผลิตภัณฑ์ทั้งสามรูปแบบนั้นมีซิลิคอนไนไตรด์เป็นองค์ประกอบหลักโดยมีลักษณะเป็นผลึก ภาพจากกล้องจุลทรรศแบบส่องผ่านแสดงให้เห็นว่าเส้นใยยาวและสารสีเทาเข้มนั้นเป็นผลึกแบบโพลีคริสตัล ในขณะที่ชั้นด้านบนที่มีลักษณะเป็นเส้นใยสั้นนั้นเป็นกลุ่มของซิลิคอนไนไตรด์ที่มีลักษณะเป็นผลึกเดี่ยว จากการทำปฏิกิริยาออกซิเดชั่นที่อุณหภูมิเปลี่ยนแปลงของผลิตภัณฑ์สีเทาเข้มนั้น พบว่าผงสีเทาเข้มนั้นประกอบด้วยคาร์บอนที่เหลืออยู่ โดยที่สามารถกำจัดคาร์บอนนั้นออกไปได้ สัดส่วนเชิงมวลของผงสีเทาเข้มจะลดลงในขณะที่สัดส่วนเส้นใยยาวสีขาวกับชั้นเส้นใยสั้นสีขาวด้านบนจะเพิ่มขึ้นเมื่อปฏิกิริยาเกิดขึ้นที่อุณหภูมิสูงขึ้นหรือช่วงเวลาที่ยาวขึ้น จากการศึกษาโดยการเปลี่ยนอัตราการไหลของก๊าซผสมสำหรับการทำปฏิกิริยา พบว่ากระบวนการนี้เกี่ยวข้องกับการกำเนิดไอของสารที่ประกอบด้วยซิลิคอน การศึกษาพบว่าก๊าซไฮโดรเจนเป็นสิ่งจำเป็นในการกำเนิดไอของซิลิคอนมอนนอกไซด์ และการโตของเส้นใย ปฏิกิริยาของก๊าซและของแข็งระหว่างไนโตรเจน คาร์บอน และ ซิลิกาถูกทำให้ดียิ่งขึ้นในกระบวนการคาร์โบเทอร์มอลรีดักชั่นและไนไตรเดชั่นของเถ้าแกลบที่ได้จากการปรับสภาพด้วยกรดก่อน นอกจากนั้นยังได้มีการศึกษากลไกการเกิดปฏิกิริยาโดยการเปรียบเทียบกับกระบวนการคาร์โบเทอร์มอลรีดักชั่นและไนไตรเดชั่นของซิลิกาบริสุทธิ์ผสมกับคาร์บอนในปริมาณที่มากเกินพอ

คำหลัก: ซิลิกอนไนไตรด์; ปฏิกิริยาคาร์โบเทอร์มอลรีดักชัน; ไนไตรเดชัน; เถ้าแกลบ

Abstract

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), which was mainly consisted of silica and carbon. 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. It was confirmed that silicon nitride was the major crystalline constituent in all product types. Transmission electron micrographs revealed that the long fiber was polycrystalline while the fibrous top layer consisted of the collection of silicon nitride single crystals. The temperature programmed oxidation of the dark gray product suggested that the dark gray powder contains residual carbon, which could be removed. Mass fraction of dark gray powder decreased, while the fraction of both white long fibers and white fibrous top layer increased when either reaction temperature or reaction duration was increased. By changing the overall flow of the gas mixture during the reaction, it was suggested that the process involves in the generation of siliceous species. Hydrogen addition was found to be essential for generation of silicon monoxide vapor and formation of fibers. Gas-solid reaction between nitrogen, carbon and silica was enhanced in the carbothermal reduction and nitridation of the acid-treated rice husk ash. Mechanism of the process was also investigated by comparing with the carbothermal reduction and nitridation of pure silica mixed with excess carbon.

Keywords: Silicon nitride; Carbothermal reduction; Nitridation; Rice husk ash

หน้าสรุปโครงการ (Executive Summary)

1. ชื่อโครงการ (ภาษาไทย) การสังเคราะห์ซิลิกอนไนไตรด์จากเถ้าแกลบ
(ภาษาอังกฤษ) Silicon Nitride Synthesis from Rice Husk Ash

2. ปัญหาที่ทำการวิจัย และความสำคัญของปัญหา

ซิลิกอนไนไตรด์เป็นเซรามิคที่เหมาะกับการใช้งานที่ต้องการความแข็งแกร่งภายใต้อุณหภูมิซึ่งสูงเกินกว่าที่โลหะสามารถทนได้ ซิลิกอนไนไตรด์นั้นมีสมบัติทางกลที่ดีหลายประการ อาทิเช่น มีความคงทนต่อการเปลี่ยนแปลงของอุณหภูมิอย่างรวดเร็ว (thermal shock) มีความแข็งแกร่ง (strength) แม้กระทั่งที่อุณหภูมิสูงและ มีความสามารถในการต้านทานการหย่อนตัว (creep) เป็นต้น นอกจากนี้ซิลิกอนไนไตรด์ยังสามารถทนต่อการกัดกร่อนจากสารเคมีหลายชนิดและสามารถทนต่อการกัดเซาะจากโลหะที่หลอมละลายได้อีกด้วย

ซิลิกอนไนไตรด์นั้นมีศักยภาพในการนำไปใช้งานมากมาย รวมถึงการใช้เป็นชิ้นส่วนของเครื่องยนต์ประสิทธิภาพสูงซึ่งทำงานที่อุณหภูมิสูงกว่าเครื่องยนต์ทั่วไป อย่างไรก็ตาม อุปสรรคอย่างหนึ่งของการนำซิลิกอนไนไตรด์ไปใช้จริงอยู่ที่ราคาการผลิตซิลิกอนไนไตรด์ซึ่งค่อนข้างสูงเกินกว่าที่จะนำไปใช้งานจริงได้ ถึงแม้ว่าการใช้ชิ้นส่วนที่ผลิตจากซิลิกอนนั้นจะทำให้การใช้เชื้อเพลิงของเครื่องยนต์มีประสิทธิภาพมากยิ่งขึ้น

การสังเคราะห์ซิลิกอนไนไตรด์วิธีหนึ่งนั้น สามารถทำได้จากกระบวนการที่เรียกว่าคาร์โบเทอร์มอลรีดักชั่น (Carbothermal reduction) ซึ่งเป็นการทำปฏิกิริยาระหว่างซิลิกา ผงคาร์บอน และก๊าซไนโตรเจนที่อุณหภูมิสูง อย่างไรก็ตาม การผสมผสานระหว่างซิลิกากับผงคาร์บอนเป็นปัจจัยสำคัญสำหรับการเกิดปฏิกิริยานี้เนื่องจากสารตั้งต้นทั้งสองอยู่ในสถานะของแข็งซึ่งไม่สามารถทำให้ผสมกันเป็นเนื้อเดียวได้โดยง่าย

แกลบเป็นผลพลอยได้จากการสีข้าวซึ่งเป็นผลผลิตหลักทางการเกษตรของประเทศไทย ถึงแม้ว่าประเทศไทยจะมีแกลบเป็นจำนวนมาก แต่ยังไม่มีการพัฒนาเพื่อเพิ่มมูลค่าให้กับแกลบอย่างจริงจัง ในปัจจุบันนี้ แกลบมักถูกใช้ประกอบการเพาะปลูกหรือใช้เป็นเชื้อเพลิงเพื่อให้ได้ความร้อนเพียงเท่านั้น

องค์ประกอบส่วนใหญ่ของแกลบตามธรรมชาตินั้นได้แก่ เซลลูโลส ลิกนิน และซิลิกา โดยที่แกลบนั้นถือได้ว่าเป็นวัสดุอินทรีย์ตามธรรมชาติที่มีซิลิกาอยู่ในประมาณมาก การเผาแกลบจะให้เถ้าที่ประกอบด้วยซิลิกาและคาร์บอนเป็นส่วนใหญ่ จะเห็นได้ว่าสารทั้งสองนี้เป็นสารตั้งต้นหลักสำหรับปฏิกิริยาคาร์โบเทอร์มอลรีดักชั่นเพื่อผลิตซิลิกอนไนไตรด์ ดังนั้นการนำเถ้าแกลบมาใช้เป็นสารตั้งต้นในการสังเคราะห์ซิลิกอนไนไตรด์จึงเป็นการประยุกต์ใช้ผลผลิตจากการเกษตรที่มีมากในประเทศ ในการผลิตผลิตภัณฑ์เซรามิกที่มีความแข็งแรงสูงที่อุณหภูมิสูงซึ่งเป็นการเพิ่มมูลค่าของแกลบได้เป็นอย่างมาก

3. สรุปย่อผลการดำเนินงานของโครงการ

โครงการวิจัยนี้เป็นการศึกษาการเพิ่มมูลค่าของแกลบโดยการนำเถ้าแกลบมาใช้เป็นสารตั้งต้นในการสังเคราะห์ซิลิกอนไนไตรด์ซึ่งเป็นเซรามิคมูลค่าสูงที่เหมาะกับการใช้งานที่ต้องการความแข็งแกร่งภายใต้อุณหภูมิซึ่งสูงเกินกว่าที่โลหะสามารถทนได้

การสังเคราะห์ซิลิกอนไนไตรด์จากเถ้าแกลบนั้นอาศัยปฏิกิริยาคาร์โบเทอร์มอลรีดักชั่นระหว่างซิลิกาและคาร์บอนซึ่งเป็นองค์ประกอบหลักของเถ้าแกลบ กับก๊าซไนโตรเจนที่อุณหภูมิสูง จากการศึกษาการทำปฏิกิริยาในปีแรกของโครงการนี้ พบว่าสามารถสังเคราะห์ซิลิกอนไนไตรด์จากเถ้าแกลบได้เมื่ออุณหภูมิของการเกิดปฏิกิริยามีค่าสูงกว่า 1400°C โดยที่ผลิตภัณฑ์ที่ได้สามารถแบ่งออกได้เป็น 3 ส่วนใหญ่ ๆ ได้แก่ เส้นใยซิลิกอนไนไตรด์สั้นซึ่งเกิดขึ้นที่ด้านบนของภาชนะใส่สารตัวอย่าง, สารผสมระหว่างคาร์บอนกับผลึกซิลิกอนไนไตรด์ในลักษณะแท่งที่ก้นของภาชนะใส่สารตัวอย่าง, และเส้นใยซิลิกอนไนไตรด์ยาวซึ่งเกิดขึ้นนอกภาชนะใส่สารตัวอย่าง โดยที่สามารถแยกผลิตภัณฑ์ในแต่ละส่วนออกจากกันได้ง่าย

ทั้งนี้ ได้มีการศึกษาการเกิดปฏิกิริยาที่อุณหภูมิต่าง ๆ ในช่วง 1300-1470°C ศึกษาการเกิดปฏิกิริยาในช่วงเวลาต่าง ๆ ตั้งแต่ 3 ถึง 10 ชั่วโมง ศึกษาอิทธิพลของความเร็วของก๊าซที่ใช้ในระบบและศึกษาผลของก๊าซไฮโดรเจนที่มีต่อการเกิดปฏิกิริยา พบว่าปัจจัยต่าง ๆ เหล่านี้ส่งผลกระทบถึงสัดส่วนของผลิตภัณฑ์ในแต่ละรูปแบบ ทำให้สามารถทราบได้ว่าการเกิดปฏิกิริยาคาร์โบเทอร์มอลรีดักชั่นนี้มีส่วนเกี่ยวข้องกับการเกิดสารตัวกลาง (intermediate) อันได้แก่ซิลิกอนมอนอกไซด์ที่อยู่ในสถานะไอ นอกจากนั้น การศึกษาผลของการเตรียมเถ้าแกลบจากแกลบดิบแสดงให้เห็นว่าการเผาแกลบให้เป็นเถ้าแกลบนั้นจำเป็นต้องถูกควบคุมให้อยู่ในสภาวะที่กำหนด มิฉะนั้นจะไม่สามารถทำปฏิกิริยาให้เกิดเป็นซิลิกอนไนไตรด์ต่อไปได้

เนื้อหางานวิจัย

1. Introduction

1.1 Silicon Nitride

Silicon nitride (Si_3N_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 (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.

Silicon nitride exists as amorphous and crystalline forms. Two common crystal structures of silicon nitride are α-phase and β-phase, both appearing to be hexagonal [Turkdogan et al., 1958]. β-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 β-silicon nitride parts usually starts from α-silicon nitride powder mixed with sintering additives which is subsequently sintered at high temperature. During sintering process, the transformation of α-phase to β-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. The overall reaction of the carbothermal reduction and nitridation of silica is as follow [Li et al., 1991; Wang and Dai, 1996]:

$$3\ SiO_2\ (s) + 6\ C\ (s) + 2\ N_2\ (g) \rightarrow Si_3N_4\ (s) + 6\ CO\ (g) \qquad (1)$$

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) is endothermic, with the heat of reaction approximately 1,268 kJ/mol Si_3N_4 at 1,427°C [Weimer et al., 1997]. Kinetically, reaction (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.

1.2 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 overall reaction (1) as mentioned earlier. However, the mechanism of the reaction is believed to involve multiple steps, where silicon monoxide acts as an intermediate [Arik, 2003]. It has been proposed that silicon monoxide is produced by reduction of silica by either carbon or carbon monoxide.

$$SiO_2\,(s) + C\,(s) \rightarrow SiO\,(g) + CO\,(g) \qquad (2)$$

$$SiO_2\,(s) + CO\,(g) \rightarrow SiO\,(g) + CO_2\,(g) \qquad (3)$$

Carbon dioxide generated from reaction (3) can further react with carbon to produce more carbon monoxide :

$$CO_2\,(g) + C\,(s) \rightarrow 2\,CO\,(g) \qquad (4)$$

Silicon nitride is then produced by reaction of silicon monoxide, nitrogen gas and either solid carbon or carbon monoxide according to reaction (5) for heterogeneous nucleation, but growth is believed to occur by a gas phase process according to reaction (6) [Weimer et al., 1997].

$$3\,SiO\,(g) + 3\,C\,(s) + 2\,N_2\,(g) \rightarrow Si_3N_4\,(s) + 3\,CO\,(g) \qquad (5)$$

$$3\,SiO\,(g) + 3\,CO\,(s) + 2\,N_2\,(g) \rightarrow Si_3N_4\,(s) + 3\,CO_2\,(g) \qquad (6)$$

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.

$$SiO\,(g) + 2\,C\,(s) \rightarrow SiC\,(s) + CO\,(g) \qquad (7)$$

Furthermore, silicon nitride can be converted to silicon carbide in the presence of carbon as well, according to reaction (8):

$$Si_3N_4\,(s) + 3\,C\,(s) \leftrightarrow 3\,SiC\,(s) + 2\,N_2\,(g) \qquad (8)$$

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

The carbothermal reduction and nitridation synthesis of α-silicon nitride is controlled by the nucleation of α-silicon nitride crystallites. The formation of α-silicon nitride nuclei occurs through a fine amorphous Si-O-C intermediate [Weimer et al., 1997]. Fine α-silicon nitride powder can be produced directly by using very fine silica. Kinetically, overall reaction is reported to be slow, requiring many hours (up to12 hours) to complete. The reaction (1) 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 reaction (2) to (6), physical contact between carbon and silica is essential for SiO vapor formation. Full conversion using a stoichiometric ratio SiO_2:C of 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.

1.3 Rice Husk

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 obstacled 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.

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. In general, silicon nitride powder can be prepared from RHA at temperature in the range of 1260 and 1500°C under a flow or nitrogen. The reaction takes place at temperature relatively lower than the conventional SiO_2/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].

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/silicon carbide composite [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. 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 intrisic 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_2/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. Experimental

2.1 Raw Materials Preparation

Rice husk used in this work was husk of jasmine rice obtained from Nakorn Ratchasima province in Thailand. For normal runs, rice husk was washed and soaked in distilled water at 90°C for 3 h to remove its impurities. Then, it was dried in an oven at 110°C for 24 h 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 in the same manner as mentioned earlier.

2.2 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).

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 h. 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]

For experiments in which the catalytic effect of various metals on the nitridation of RHA was investigated, metal impregnated RHA was prepared by immersing about 2 g of RHA in 10 mL of solution of metal nitrate compounds in methanol, followed by natural evaporation of all methanol at room temperature. Metals investigated in this work were iron and aluminum. The content of metal impregnated was adjusted to be 0.5%, 1.0% and 3.0%wt. respectively, based on mass of reduced metal. The sample was put into an oven at 110°C for 24 h to ensure the elimination of all possibly remaining methanol and moisture.

2.3 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. 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.

2.4 Characterization of the Products

Crystalline phases of the product were determined from X-ray diffraction analysis, using a SIEMENS D5000 diffractometers with CuKα radiation. The functional groups in the samples were determined by using a Nicolet Impact 400 infrared spectrometer, whereas the sample was mixed with KBr and formed into a thin pellet before measurement. The residual carbon content and thermal behaviors of the samples were determined by using TG/DTA analysis on a Diamond TG/DTA thermogravimetric instrument. Finally the morphology of the products was examined by using a scanning electron microscope (JSM-6400 JEOL Co., Ltd.) and a transmission electron microscope (JEM-2010, JEOL Co., Ltd.). The crystallographic information was also obtained from the selected area electron diffraction (SAED) analysis performed in the same instrument.

3. Results and Discussion

3.1 General Observations for the Carbothermal Reduction and Nitridation of RHA

It was observed from the experimental results that the products of the reaction can be generally 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).

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 1 and Figure 2 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 2θ of 34.92° and 35.68° 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 (2θ of around 35.75°) might be overlapped. It should be noted that silicon nitride in both DGP and WFM layer are α-Si_3N_4 with no trace of β-Si_3N_4. On the contrary, the XRD peak of CWF portion reveals the present of β-Si_3N_4 in addition to α-Si_3N_4.

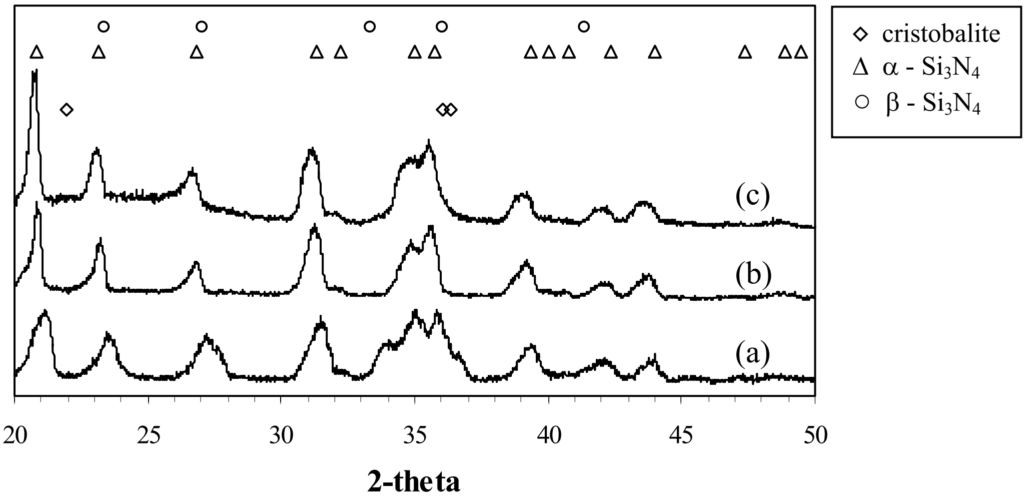


Figure 1 XRD patterns of products from the carbothermal reduction and nitridation at 1450°C for 6h:

(a) cotton-like white fibers on the edge of sample holder (CWF)

(b) white fibrous top layer (WFM)

(c) dark gray powder (DGP)

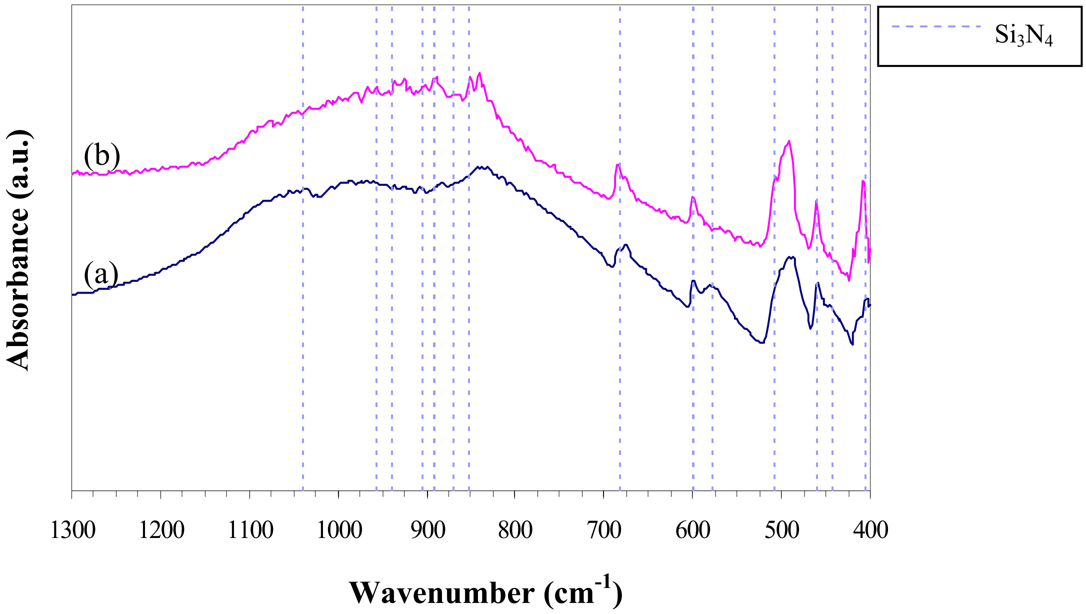


Figure 2 IR patterns of product from the carbothermal reduction and nitridation at 1450°C for 6 h:

(a) cotton-like white fibers on the edge of sample holder (CWF)

(b) white fibrous top layer (WFM)

Characterization of the product obtained was also conducted by X-ray Photoelectron Spectroscopy (XPS). The results, shown in Table 1 confirm that all product types contain silicon, nitrogen and oxygen.

Table 1 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 3. 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 equipped 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 mm, thickness in sub-micron scale and length of several hundred micrometers. The tip of the ribbon is beveled 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 Si_3N_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 mm. 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 reaction 6. No sign of liquid, e.g. melting or bead forming at the tip of the fiber, was observed from SEM images (Figure 3a). This is indicated that the fiber grows by VS mechanism, rather than VLS mechanism.

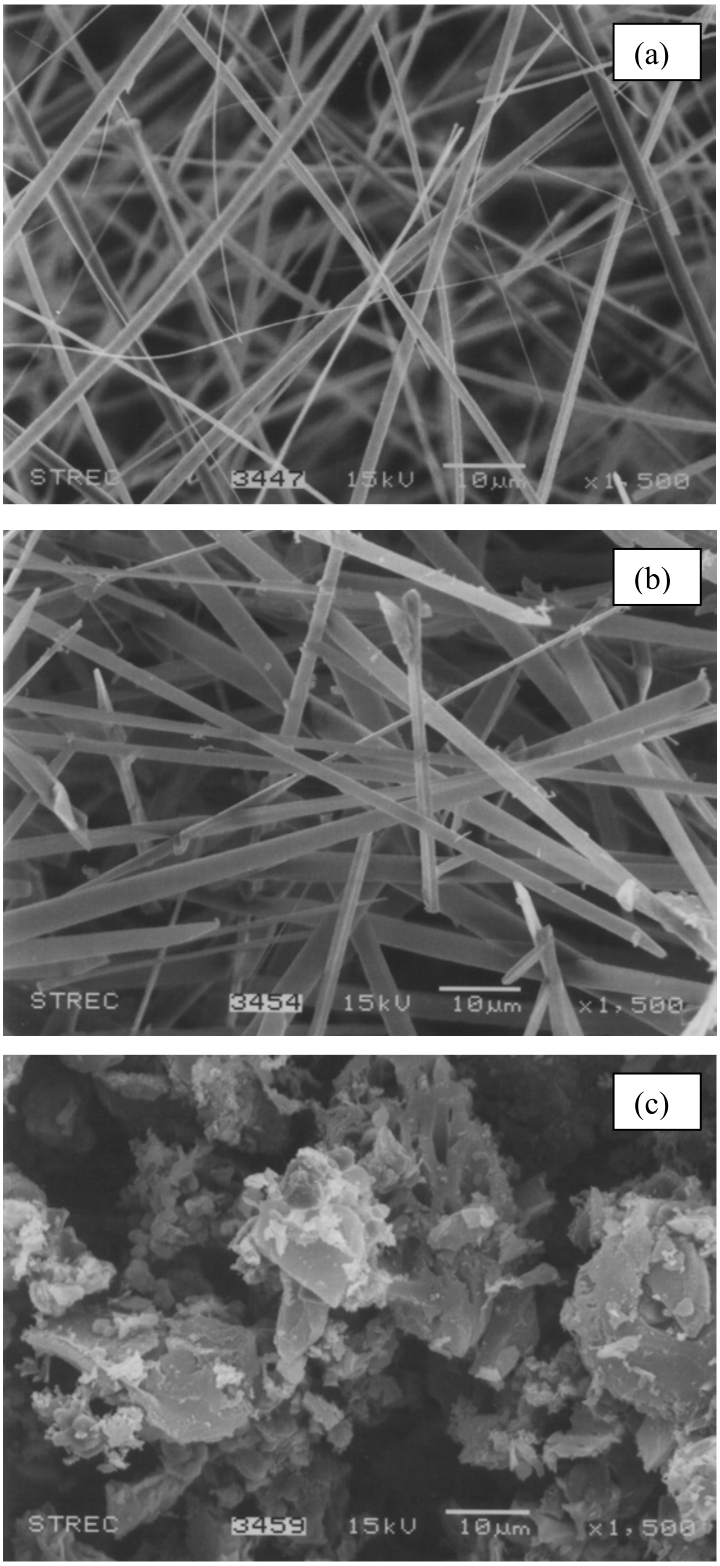


Figure 3 SEM micrographs of products from the carbothermal reduction and nitridation at 1450°C for 6h: (a) cotton-like white fibers on the edge of sample holder (CWF), (b) white fibrous top layer (WFM), (c) dark gray powder (DGP).

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 2 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 and 5, 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.

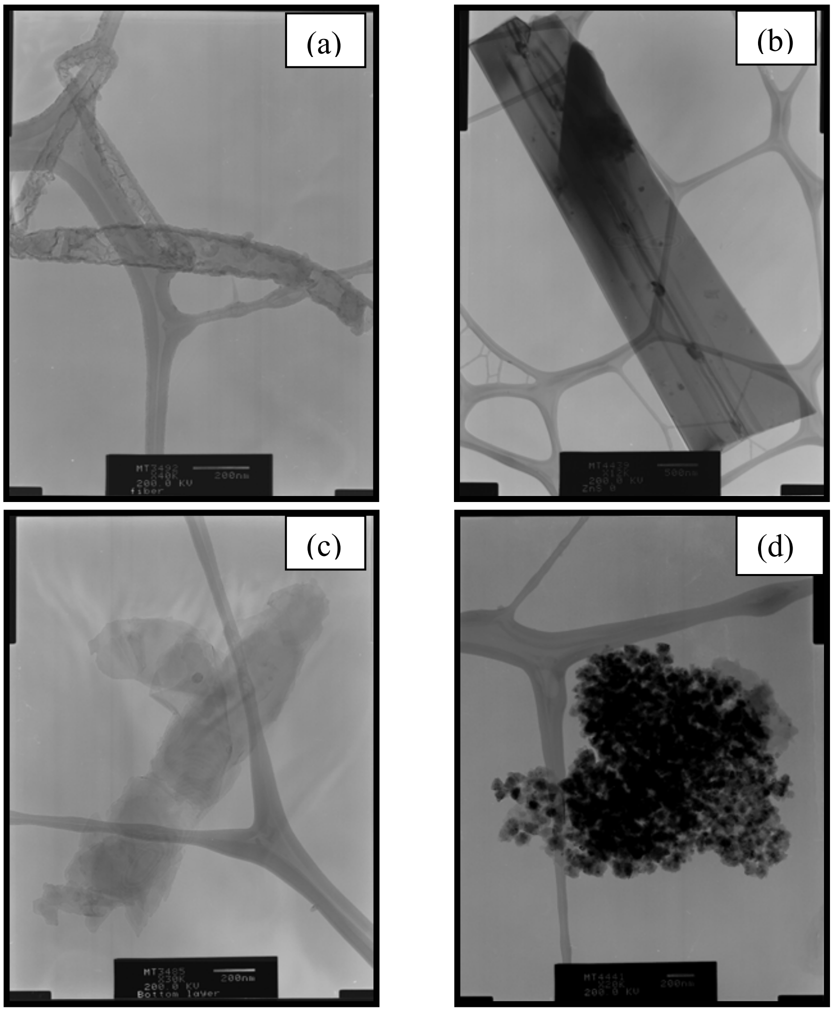


Figure 4 TEM micrographs of products from the carbothermal reduction and nitridation at 1450°C for 6 h:

(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)

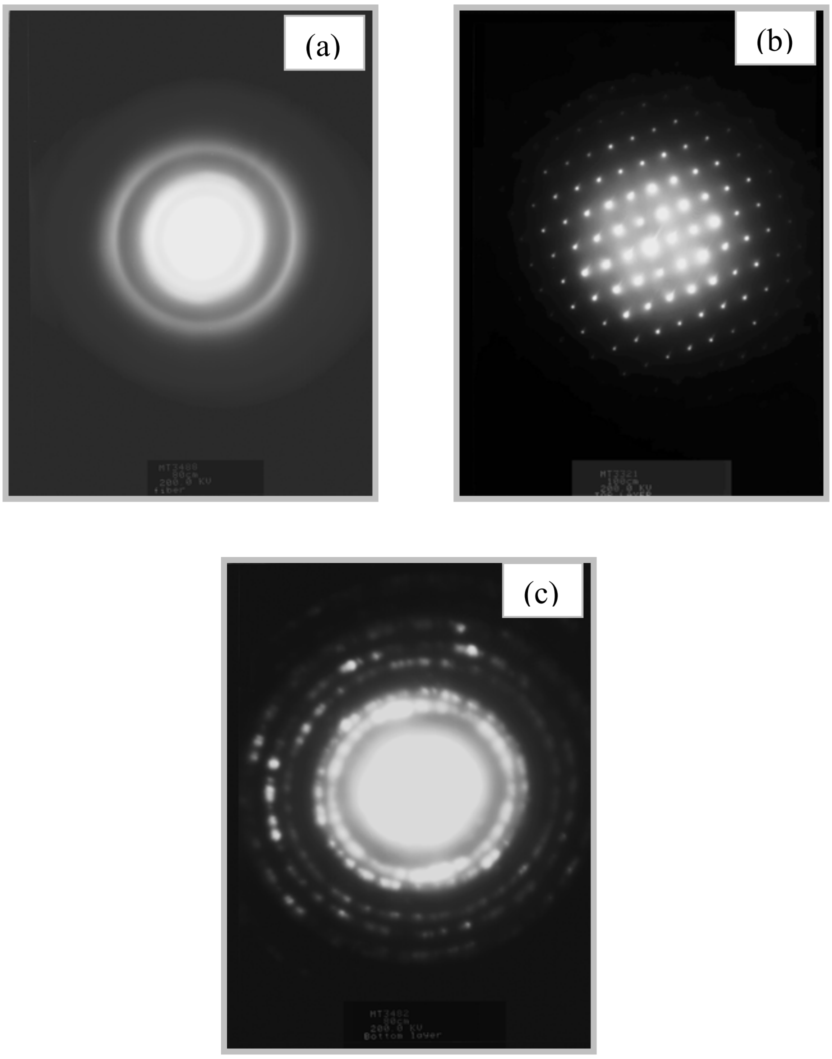


Figure 5 SAED patterns of products from the carbothermal reduction and nitridation at 1450°C for 6 h:

(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)

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 3. 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 carbon monoxide as shown in Eq. 2 and 3. 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 3 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[(a)] (%)	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

(a) Minus sign indicates mass loss after the carbothermal reduction and nitridation process.

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 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. 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.

3.2 Effect of Reaction Temperature

Effect 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.

Table 4 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 (a)	Sample mass change(b) (%)	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

(a) 1 represents sample in the upstream sample holder, while 2 represents sample downstream.
(b) 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 reaction 2. 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.

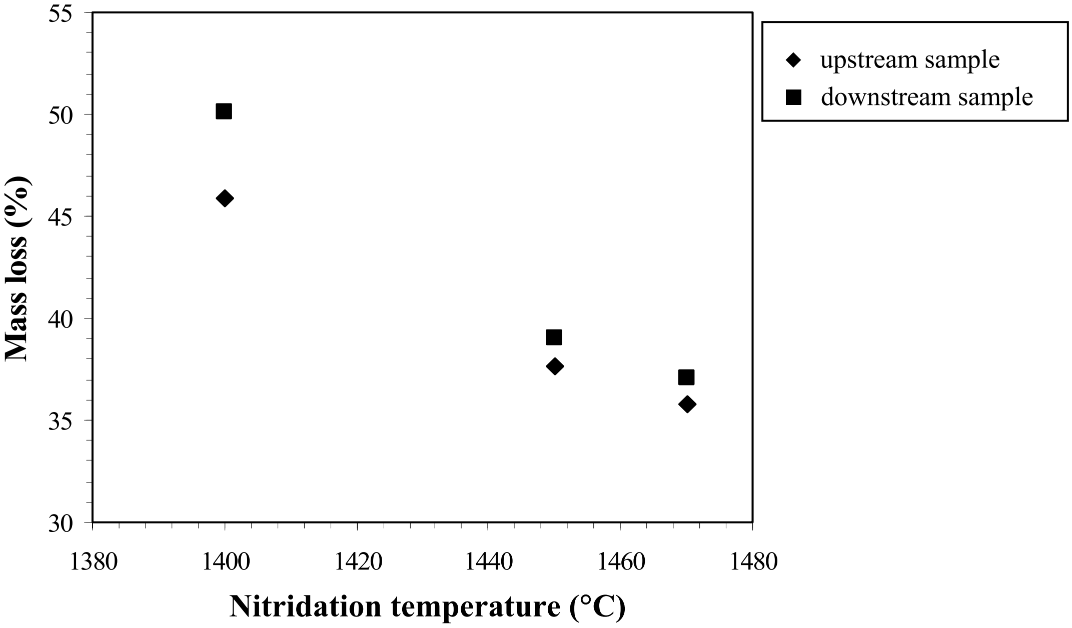


Figure 6 Results from TG/DTA analysis for the DGP portion of product synthesized at various temperatures.

The result in Figure 6 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 (reaction 2) or carbon monoxide (reaction 3). In spite of being thermodynamically less favored than reaction 2, some authors have assumed that reaction 3 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 due to silica and carbon contact is significantly reduced. Therefore, Eq. 2 may also play an important role in the nitridation process of RHA.

3.3 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 5.

Table 5 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 $^{(a)}$	Sample mass change$^{(b)}$ (%)	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

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 β-SiC or Si_2N_2O 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_2 to form Si_3N_4.

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 6.

Table 6 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_2 (%)	No. of sample tray (a)	Sample mass change(b) (%)	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

(a) 1 represents sample in the upstream sample holder, while 2 represents sample downstream.

(b) 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_2 atmosphere is silica in cristobalite phase with no silicon nitride.

Amount of fibers in CWF portion increases when the concentration of hydrogen is increased. 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. 9 and increase the yield of the reaction between silica and carbon.

$$SiO_2\,(s) + H_2\,(g) \rightarrow SiO\,(g) + H_2O\,(g) \qquad (9)$$

It should be note 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.

3.4 Effect 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 7. 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 7 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 [(a)]	Sample mass change[(b)] (%)	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

(a) 1 represents sample in the upstream sample holder, while 2 represents sample downstream.
(b) Minus sign indicates mass loss after the carbothermal reduction and nitridation process.

3.5 Effect 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 8, reveal that SiO_2 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, 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 8 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 are shown in Figure 7 and Figure 8, respectively. 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. 1 is enhanced in case of ATRH. This may be the result from the enhanced surface area of ATRH, implying from the results reported in literatures. The XRD patterns of products in each portion confirm that silicon nitride is the major crystalline phase in all product types. No other apparent crystalline phase is detected.

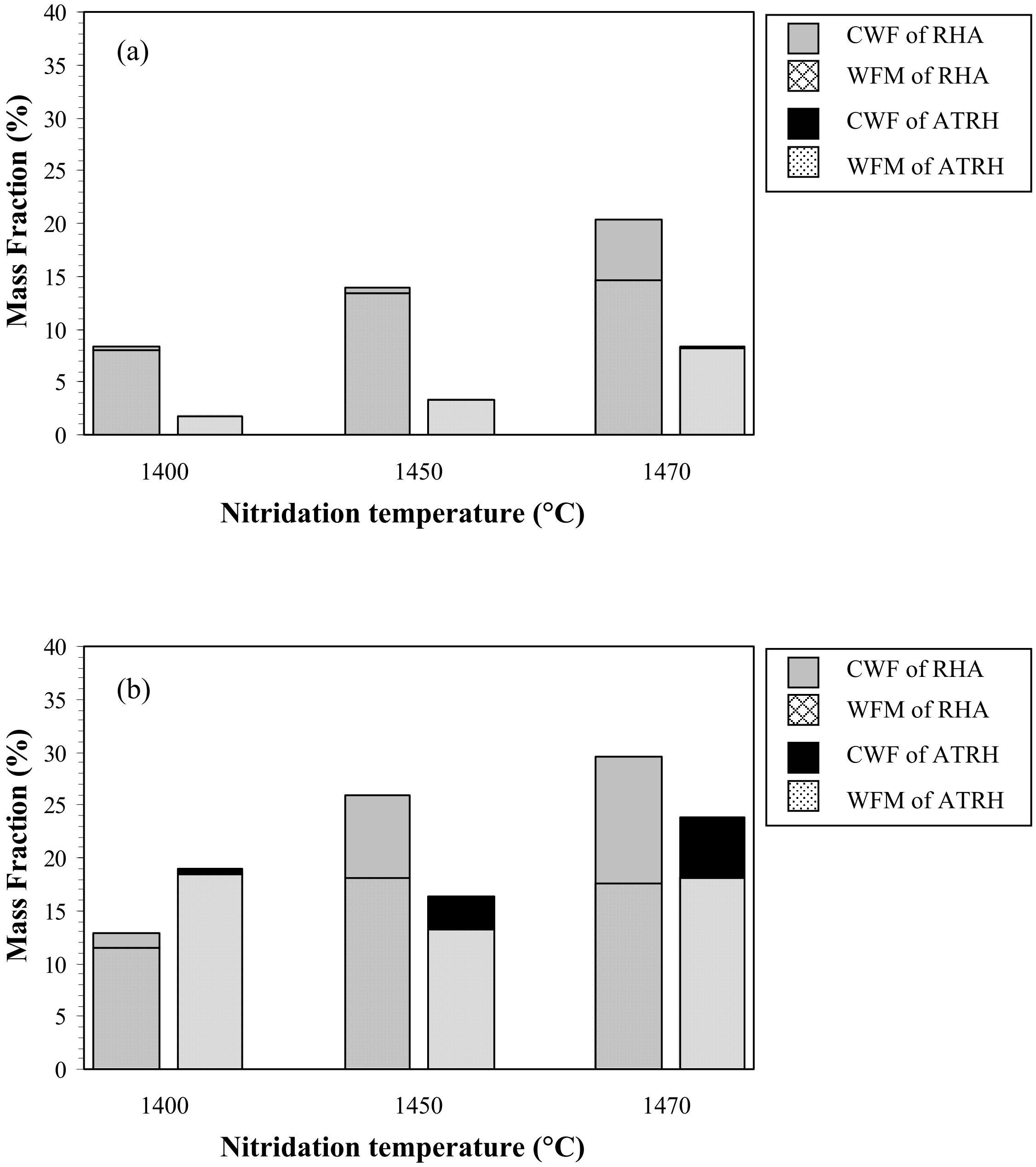


Figure 7 Comparison of mass fraction of CWF and WFM layers of products obtained from the nitridation of RHA and ATRH at various temperatures:

(a) products in upstream sample holder

(b) products in downstream sample holder

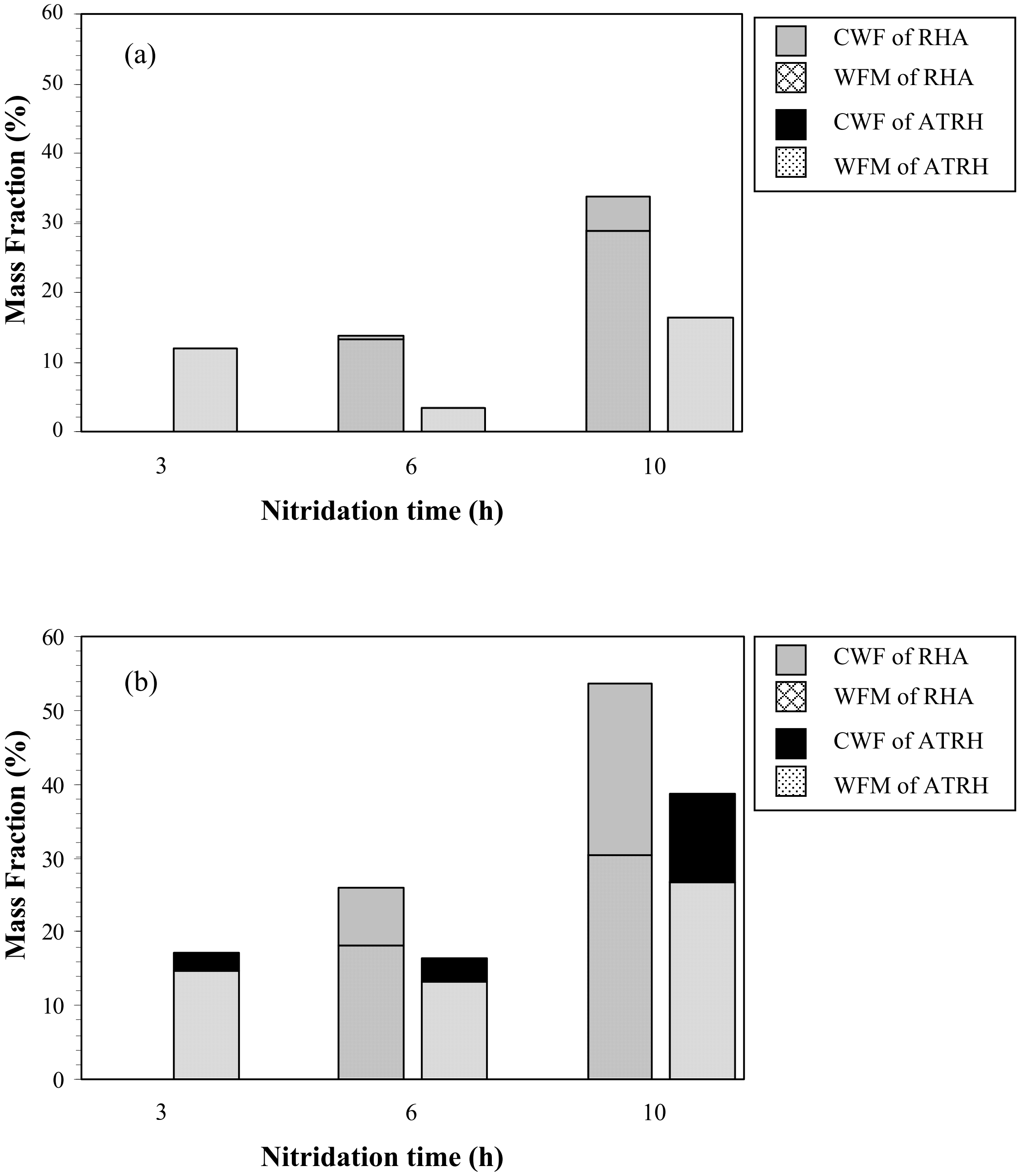


Figure 8 Comparison of mass fraction of CWF and WFM layers of products obtained from the nitridation of RHA and ATRH at various times:

(a) products in upstream sample holder

(b) products in downstream sample holder

3.6 Comparative Study using Silica Physically Mixed with 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 9.

Table 9 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 [(a)]	Sample mass change[(b)] (%)	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	-

[(a)] 1 represents sample in the upstream sample holder, while 2 represents sample downstream.
[(b)] 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 9 and 10 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 temperature for the carbothermal reduction and nitridation 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.

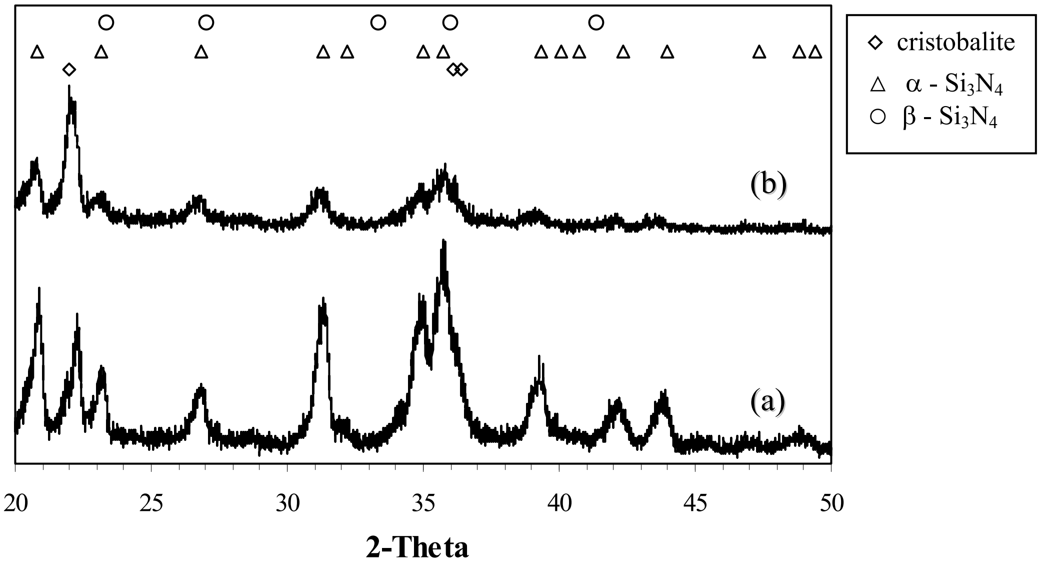


Figure 9 XRD patterns of products from the carbothermal reduction and nitridation of silica mixed with excess carbon at 1450°C for 3 h:

(a) white fibrous top layer (WFM)

(b) dark gray powder (DGP)

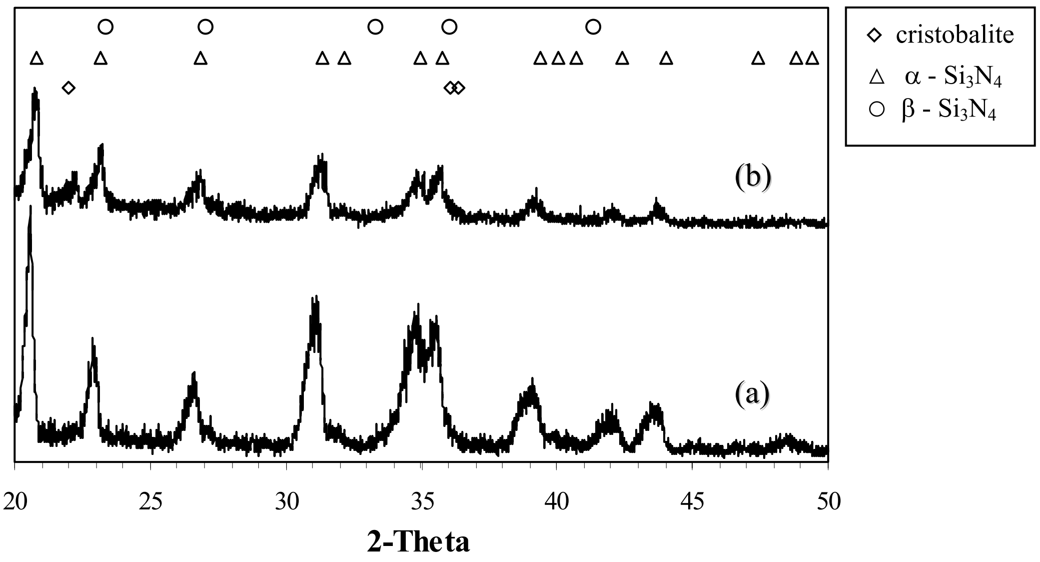


Figure 10 XRD patterns of products from the carbothermal reduction and nitridation of silica mixed with excess carbon at 1450°C for 6 h:
(a) white fibrous top layer (WFM)
(b) dark gray powder (DGP)

3.7 Catalytic Effects of Iron

Iron is investigated in this work because it has been found to be effective in term of enhancing the formation of β-silicon nitride in the direct nitridation of silicon [Pigeon et al., 1993]. The effect of iron on the carbothermal reduction and nitridation of RHA is shown in Figure 11. It indicates that iron affects the reaction such that it enhances the β-phase formation. It should be noted that neither WFM nor DGP layers was observed from the nitridation of iron-impregnated RHA. Figure 11 shows the tendency in decreasing the fraction of α-phase with an increase in the amount of iron addition. In this work, the maximum fraction of β-phase obtained from iron impregnated sample is 74.5%, when the content of iron is 3% by mass.

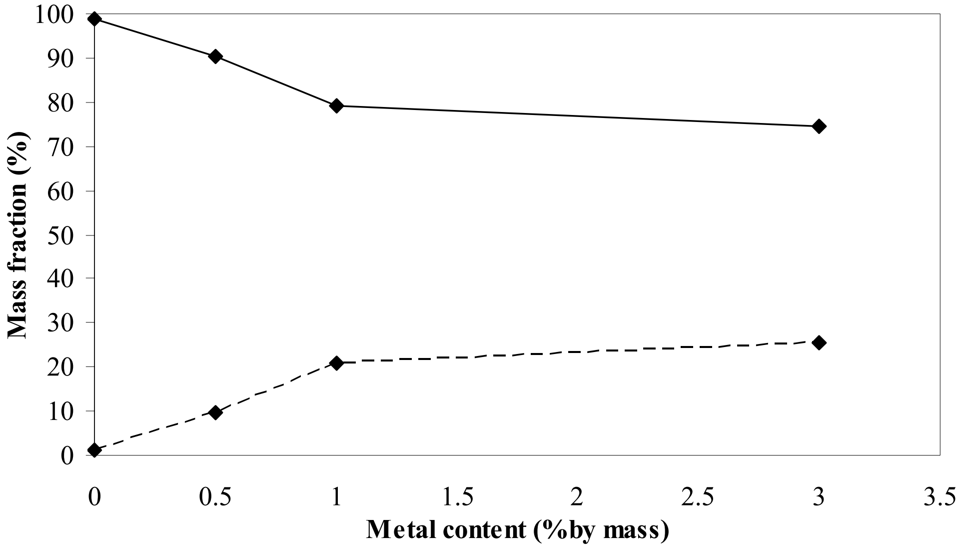


Figure 11 Fraction of α- and β-phase in silicon nitride obtained from the carbothermal reduction and nitridation of RHA impregnated with iron at 1450°C for 6 h: (—) α-phase; (---) β-phase.

According to results from XRD analysis, iron not only promotes β-silicon nitride formation, but also enhances silicon carbide. This effect is very strong when amount of iron impregnated to RHA is increased. Nevertheless, the TG/DTA analysis of the nitrided samples as shown in Figure 12 indicates that amount of residual carbon in the sample decreased with an increase in iron content. It means that the reaction between silica and carbon in RHA is enhanced by the presence of iron. It is suspected that the formation of silicon carbide in addition to silicon nitride further consumed carbon in the system. Therefore, it results in less carbon remaining in sample. The fact that silicon carbide was obtained from iron impregnated RHA supports with the report in literatures that iron promotes silicon carbide over silicon nitride [Siddiqi et al., 1985].

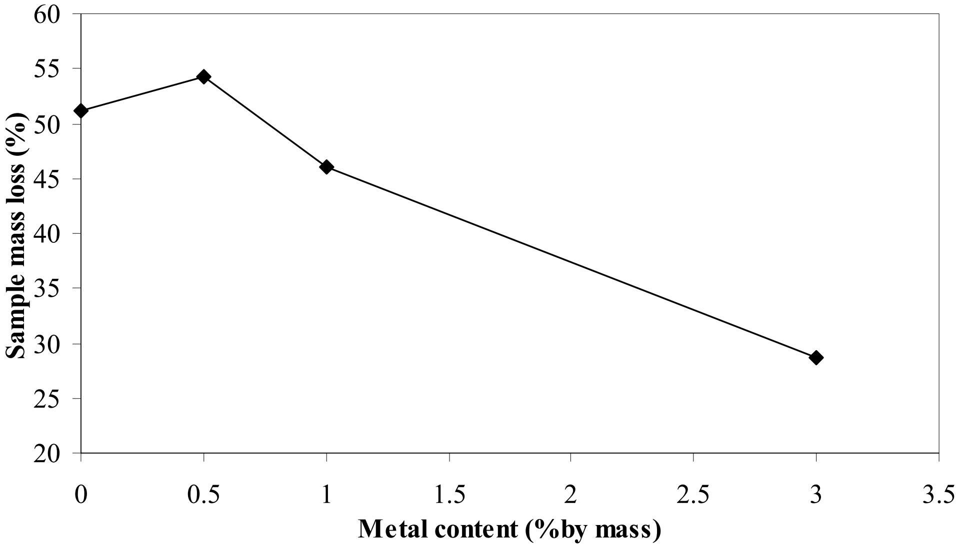
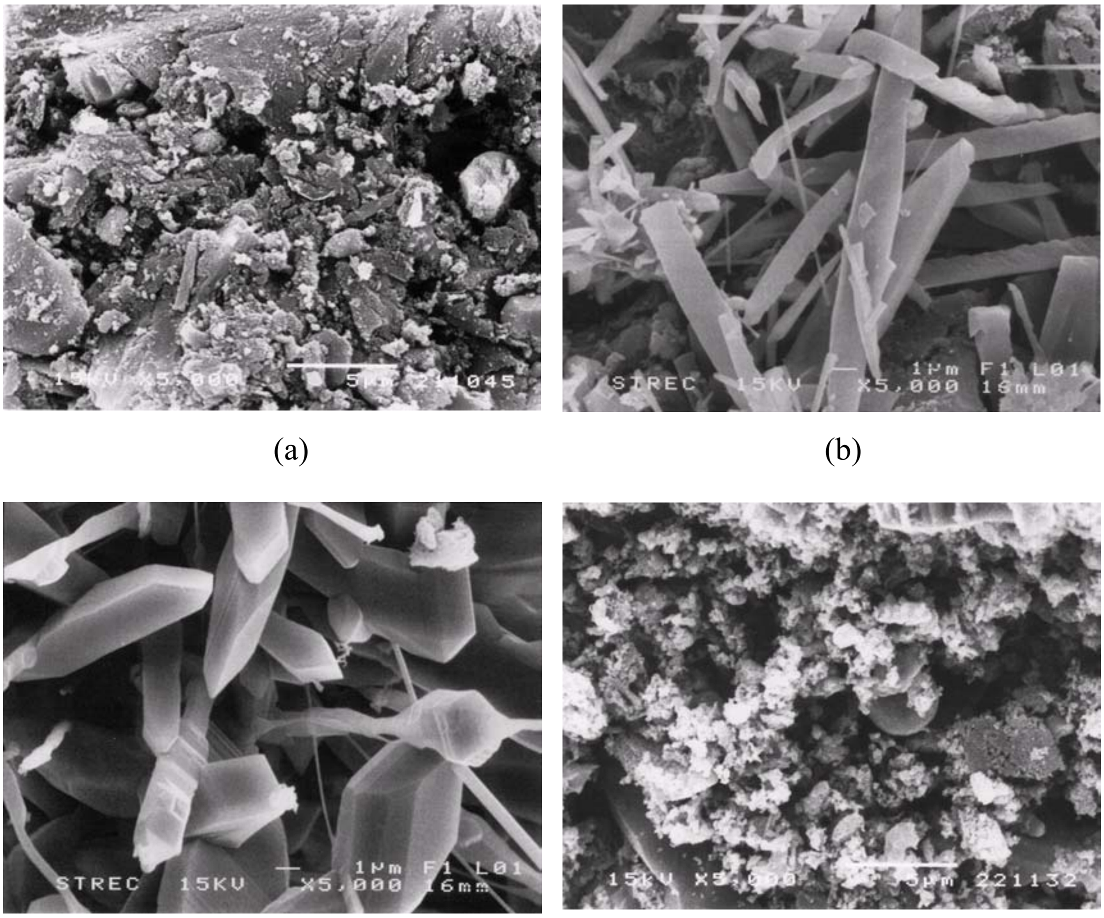


Figure 12 Results from TG/DTA analysis of the product from the carbothermal reduction and nitridation of RHA impregnated with iron at various concentrations.

The SEM micrographs of the nitrided product are shown in Figure 13. Since the nitrided product of iron-impregnated RHA was not consisted of two distinguishable portions, only the SEM image for bottom portion of the nitrided product of the unimpregnated RHA is used as the reference. For 0.5, 1.0 and 3.0% iron impregnated RHA, the nitrided product are shown in Figure 13(b), 13(c) and 13(d), respectively. It can be described that when amount of iron impregnated to RHA is increased, grains in silicon nitride product are generally much bigger than that in sample with low content of iron. However, for 3.0% iron content, the morphology is significantly different because the product is predominantly silicon carbide.



(a) (b)

(c) (d)

Figure 13 SEM micrographs of products from the carbothermal reduction and nitridation at 1450°C for 6 h of:

(a) unimpregnated RHA

(b) RHA impregnated with 0.5% iron

(c) RHA impregnated with 1.0% iron

(d) RHA impregnated with 3.0% iron

Results from XRD analysis of the iron-impregnated RHA nitrided for different period of time are shown in Figure 14. It is indicated that silicon carbide is the dominant product at the beginning of the carbothermal reduction and nitridation process. Then, the formation of silicon nitride is favored as the reaction proceeds. It means that silicon carbide is converted to silicon nitride, which is a reverse reaction of reaction (8).

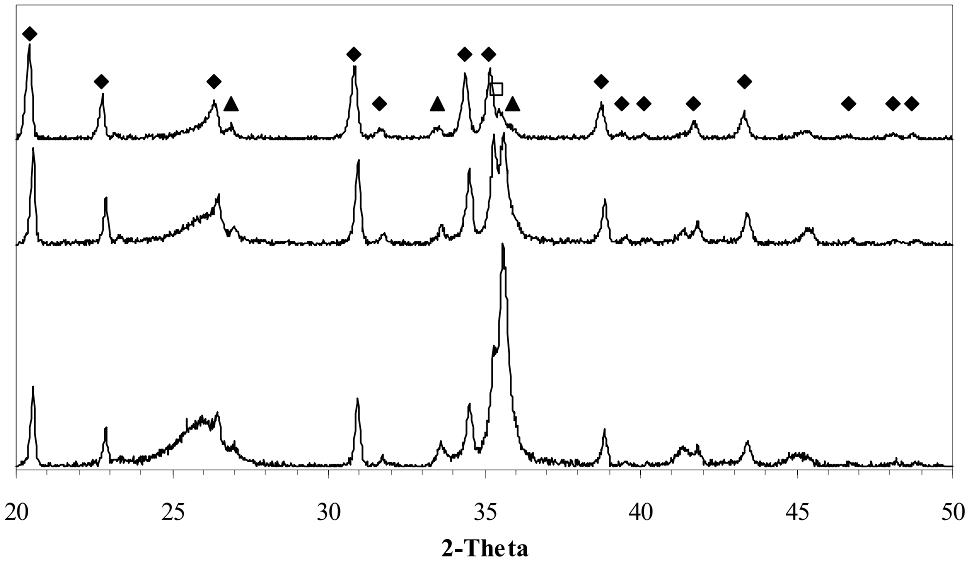


Figure 14 XRD patterns of products from the carbothermal reduction and nitridation of RHA impregnated with iron under various reaction times: (◆) α-Si_3N_4, (▲) β-Si_3N_4, (□) SiC.

4. Conclusion

Silicon nitride is successfully synthesized from rice husk ash via the carbothermal reduction and nitridation process at temperature higher than 1400°C. There are three forms of product observed, i.e. dark gray powder of silicon nitride grains mixed with residual carbon, a layer of white fibrous material which is in fact rod-like shaped silicon nitride, and cotton-like silicon nitride long fibers. No other crystalline phase was detected. Although carbonaceous compound remains in the product, it can be removed by an oxidation process. The formation of cotton-like fibers outside the cavity of the sample holder suggests that the process involves the reaction in vapor phase.

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Output ที่ได้จากโครงการ

1. การนำเสนอผลงานในประชุมวิชาการ The First Workshop on the Utilization of Rice Husk and Rice Husk Silica ซึ่งจัดโดยศูนย์เทคโนโลยีโลหะและวัสดุแห่งชาติ ในวันที่ 19 กันยายน 2548 ภายใต้หัวข้อ Effects of Rice Husk Pretreatment on the Formation of Silicon Nitride from Rice Husk Ash (ได้แสดง Proceeding ไว้ในภาคผนวก ก.)
2. บทความทางวิชาการเรื่อง Effects of Reaction Parameters on Carbothermal Reduction and Nitridation of Rice Husk Ash for Silicon Nitride Synthesis ซึ่งกำลังจัดส่งไปยังวารสาร Ceramics International (ได้แนบ manuscript ไว้ในภาคผนวก ข.)

ภาคผนวก ก.

Proceeding ของการประชุมวิชาการ The First Workshop on the Utilization of Rice Husk
and Rice Husk Silica ซึ่งจัดโดยศูนย์เทคโนโลยีโลหะและวัสดุแห่งชาติ
ในวันที่ 19 กันยายน 2548

ภาคผนวก ข.

Manuscript ของบทความทางวิชาการเรื่อง Effects of Reaction Parameters on Carbothermal Reduction and Nitridation of Rice Husk Ash for Silicon Nitride Synthesis